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Metallographische Untersuchung über das System von Antimon und Tellur.

VON

Yasukiyo Kimata.

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Über die Legierungen von Antimon und Tellur scheinen bisher nur folgende Angaben veröffentlicht zu sein. Oppenheim[1] stellte dar, dass Antimon und Tellur die eiserne graue Verbindung SbTe und die zinnerne weisse Sb_2Te_3 bilden. Werner Haken[2] bestätigte die Existenz der letzten Verbindung durch die Untersuchung über die thermoelektrischen Eigenschaften der Legierungen und stellte dar, dass der U-förmige Verlauf der Thermokraft zwischen Sb und Sb_2Te_3 für das Auftreten von Mischkristallen charakteristisch ist. Pélabon[3] erhielt eine Verbindung Sb_2Te_3 durch die direkte Erhitzung von Antimon und Tellur, deren Schmelzfluss mit dem Überschuss der beiden Komponenten mischbar ist. Die Schmelzkurve ist W-förmig ; das Maximum der Erstarrungstemperaturen entspricht der Bildung der Verbindung Sb_2Te_3 ; das eine Minimum steht in Beziehung zur Solidification des eutektischen Gemisches 5 Sb : 2 Te, und das andere zur Solidification des eutektischen Sb : 10 Te. Fay und Ashley[4] untersuchten das System auf dem thermischen Wege, um zu entscheiden, ob Antimon und Tellur mit einander isomorph seien oder nicht. Damals haben sie das Schmelzdiagramm, welches ich zum Vergleiche in meinem Diagramme mit feineren Linien wiedergebe, abgeleitet, und sie kamen zum Schlusse, dass Sb_2Te_3 und Te ein Eutektikum, und Sb_2Te_3 und Sb miteinander die Reihen der Mischkristalle bilden.

Nun scheint uns die Bildung der Verbindung Sb_2Te_3 fast ohne Zweifel zu sein ; doch bleibt die Entstehung der zweiten Verbindung SbTe noch gar nicht bestätigt. Ob die Verbindung Sb_2Te_3 sich mit

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1 J. prakt. Chem., **71**, 277 (1857).
2 Chem. Zentralbl., **81**, 1694 (1910).
3 C. R., **142**, 207 (1906).
4 Amer. Chem. J., **27**, 95 (1902).

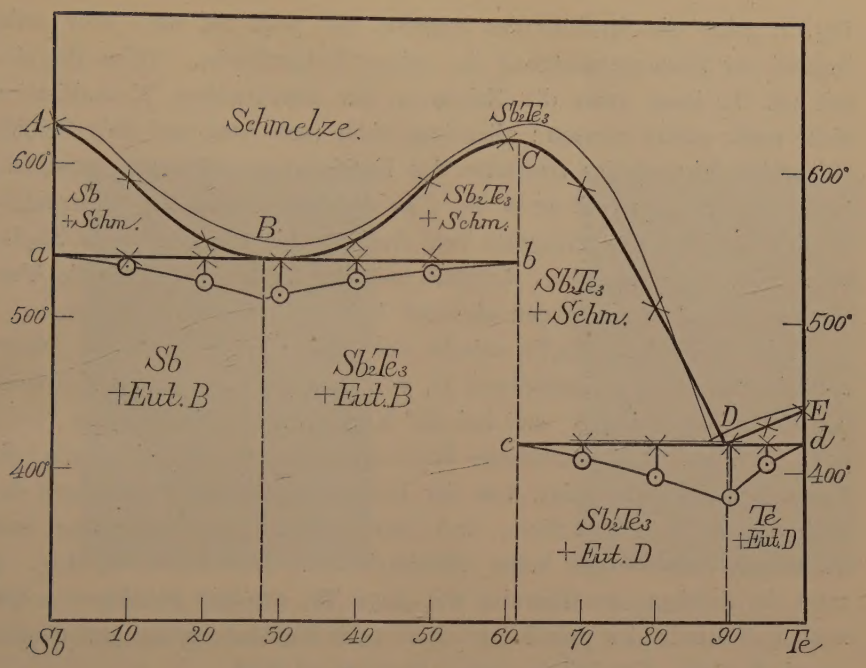
Antimon im festen Zustande mischt, ist auch noch nicht entschieden, wie die bisherigen Angaben darüber sehr von einander abweichen. Sonach habe ich im Folgenden diese verschiedenen Fragen durch die thermische Analyse zu lösen gesucht.

Zur Schmelzung der Legierungen benutzte ich die Meissner Porzellanröhre; das Gesamtgewicht der beiden Komponenten betrug bei allen Versuchen stets 20 g. Sie wurden unter einem langsamen Kohlensäurestrome mit Hilfe eines Bunsenbrenners geschmolzen. Zur Temperaturmessung bediente ich mich des Platin- Platinrhodiumthermoelementes von Heraeus, und immer, bevor die wirkliche Messung geschah, wurde die Schmelze sorgfältig gerührt, um die vollkommene Homogenität der Mischung erhalten zu können. Die Abkühlung der Schmelze wurde dadurch möglichst verlangsamt, dass das Schmelzrohr in ein cylindrisches Sandbad, und dieses wieder in einen Asbestcylinder von doppelt so grossem Durchmesser, welcher während der Abkühlung von unten durch eine mit Sand gefüllte Eisenschale und von oben mit einer Asbestplatte sorgfältig geschlossen wurde, gebracht wurde. Jede Abkühlungskurve wurde zweimal bestimmt; aus den gefundenen Temperaturen wurde das Mittel genommen.

Die Resultate der Versuche sind in Tabelle I zusammengestellt, und auf Grund deren ist das Zustandsdiagramm entworfen. Die Temperaturen sind im Massstabe von 5° = 1 mm. wiedergegeben.

Tabelle I.

Versuchs-nummer	Te-Gehalt in Gew.- %	Temperatur d. Beginns d. Krist. in °C,	Eutektische Kristallisation	
			Temp. in °C.	Zeitdauer in Sek.
1	100	Schmelzpunkt des Tellurs: 442°		
2	95	431	421	165
3	90	427	420	400
4	80	551	418	240
5	70	592	419	150
6	60	620	—	—
7	50	595	545	95
8	40	551	541	155
9	30	442	542	280
10	20	552	539	190
11	10	590	540	80
12	1	625	—	—
13	0	Schmelzpunkt des Antimons: 627°		



Gew. % d. Tellurs.

Wie aus dem Diagramm ersichtlich, besteht die Schmelzkurve aus drei Ästen AB, BCD und DE mit einem Maximum C und noch mit zwei eutektischen Horizontalen *ab* und *cd*.

Das Maximum C liegt bei ca. 620° und bei der Konzentration von 61·41% Te. Hier muss eine Verbindung mit der Formel Sb_2Te_3 gebildet werden. Dementsprechend ist die Struktur eines Schliffes von diesem Regulus ganz homogen, wie das Lichtbild, Fig. 1, zeigt. Die Verbindung Sb_2Te_3 mischt sich nicht im festen Zustande mit Antimon, und so bildet sie mit dem lelzten ein Eutektikum. Der Kurve AB entlang beginnt sich Antimon aus der Schmelze primär auszuscheiden. Die Temperatur des Beginns der Kristallisation fällt allmählich mit der zunehmenden Menge des Tellurs von 627° bis zu 540° ab. Der Kurve BC entlang beginnt sich die Verbindung primär auszuscheiden, während die Temperatur von 620° endlich auch bis zu 540° fällt. Bei der letzten Temperatur erstarrt der Rest der Schmelze zum Eutektikum in allen Konzentrationen von 0% bis 61·41% Te. Aus der Kurve der Zeitdauer der eutektischen Kristallisation lässt sich das Maximum als auf 27—28% Te liegend berechnen, sodass das reine Eutektikum B aus 46 Teilen Sb_2Te_3 und 54 Teilen Sb bestehen muss. Das Lichtbild,

Fig. 2, zeigt die Struktur des Regulus mit 30% Te, also sehr nahe liegend zur Zusammensetzung des reinen Eutektikums. Beim Regulus mit 1% Te kann man die Zeitdauer der eutektischen Kristallisation nicht mehr genau messen ; allerdings sieht man noch auf dem Schliffe (Lichtbild, Fig. 3) das Auftreten des Eutektikums. Dasselbe geschieht auch beim Regulus mit 60% Te. Infolgedessen muss die Horizontale *ab* sich von der Konzentration von Antimon bis nach der von Sb_2Te_3 erstrecken. So folgt, dass Antimon mit der Verbindung und die Verbindung mit Antimon gegen einander keine Mischkristalle bildet.

Die Verbindung Sb_2Te_3 mischt sich auch nicht mit Tellur ; daher entsteht ein zweites Eutektikum D, von dem die maximale Zeitdauer der Erstarrung bei 420° und bei der Konzentration ein Bischen unter 90% Te liegt. Die eutektische Horizontale *cd* erstreckt sich, wie die Kurve der Zeitdauer zeigt, von der Konzentration der Verbindung bis nach der des reinen Tellurs, und daher bilden die Verbindung und Tellur mit einander gar keine Mischkristalle. Das Lichtbild, Fig. 4, zeigt die Struktur des Regulus mit 70% Te, wo die dunkler erscheinenden Kristalle der primär ausscheinenden Verbindung entspricht, und dazwischen das Eutektikum weiss erscheinend liegt.

Zusammenfassung :

1. Tellur und Antimon bilden miteinander nur eine Verbindung Sb_2Te_3.
2. Diese Verbindung schmilzt bei ca. 620°.
3. Diese Verbindung bildet die Eutektika mit Antimon ebenso gut wie mit Tellur.

Zum Schluss, sei mir gestattet, Herrn Prof. Dr. M. Chikashige für seinen freundlichen Rat und Beistand meinen Dank auszusprechen.

Fig. 1. Regulus m. 61.4% Te; m. warmer verd. HNO_3 geätzt. 168 fache Vergr.

Fig. 2. Regulus m. 30% Te; m. warmer verd. HNO_3 geätzt. 168 fache Vergr.

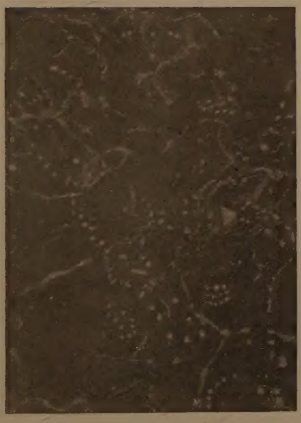


Fig. 3. Regulus m. 1% Te; m. warmer verd. HNO_3 geätzt. 168 fache Vergr.

Fig. 4. Regulus m. 70% Te; m. warmer verd. HNO_3 geätzt. 168 fache Vergr.

Metallographische Untersuchung über das System von Tellur und Selen.

VON

Yasukiyo Kimata.

(Eingegangen am 16. Februar 1915.)

Über die Legierungen von Tellur und Selen liegt bisher nur die Arbeit von W. Haken[1] vor. In ihr misst der verfasser die Werte der Thermokraft und der elektrischen Leitvermögen für die Legierungen mit 98—50% Te-Gehalte.

Im Folgenden habe ich durch die thermische Analyse, wie gewöhnlich, zu untersuchen versucht, welche Verbindungen die beiden Elemente mit einander eingehen.

Das von mir gebrauchte Tellur war dasselbe wie das in der vorigen Arbeit. Das Selen zeigt eine grosse Tendenz glasig zu erstarren; um es im kristallisierten Zustande zu gewinnen, musste ich die Schmelze so langsam abkühlen lassen, dass die Temperaturen von 250° bis mehr als 50° im Laufe einer Stunde sanken. So kristallisiert das Selen nach einer starken Unterkühlung erst bei 197°. Die glasig werdende Tendenz beobachtet man auch bei der Erstarrung der Selen-reicheren Reguli; man hat also dieselbe Mühe anzuwenden wie beim Selen, um sie kristallisieren lassen zu können.

Als Heizofen benutzte ich einen Graphittiegel ohne Boden, in dem ich das Schmelzrohr einsetzte; nach dem Schmelzen wurde der Ofen von oben ebenso wie von unten mit Asbestplatten bedeckt. Bei einer solchen Einrichtung wurde die Abkühlungsgeschwindigkeit so vollkommen reguliert, wie gewünscht. Zur Temperaturmessung bediente ich mich eines Konstantan-Silberthermoelementes mit Eichung von der Deutschen Reichsanstalt.

Die Resultate der Versuche sind in Tabelle I zusammengestellt, und auf Grund deren ist das Zustandsdiagramm entworfen.

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1 Ann. Physik, [4], **32**, 330 (1910).

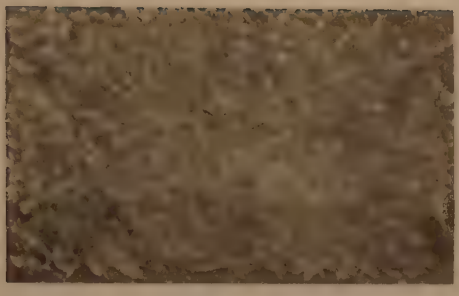

Fig 1. Regulus m. 50% Se;
m. verd. KOH geätzt. 168 f. Vergr.

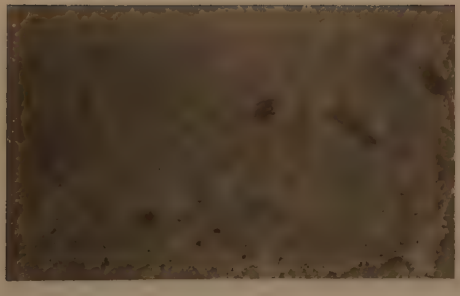

Fig. 2. Regulus m. 97% Se;
m. verd. KOH geätzt. 168 f. Vergr.

Studies in the Stereochemistry of Quinquevalent Nitrogen. II.

Resolution of the Asymmetric Quarternary Ammonium Compounds.

By

Shigeru Komatsu.

(Received February 23, 1915.)

The author has already shown in his previous article[1], that the four negative valences of the nitrogen atom in the quarternary ammonium compounds are of the same value, but it has still remained as a question that the melting point of compound formed by one and the same method is different in the statements of different investigators.

Hence, the present work was undertaken to decide whether the author's substance is a true asymmetric compound or not, and at the same time to study the spatial configuration of atoms or atomic groups in the molecule.

Pure methyl n-propyl phenyl benzyl ammonium iodide prepared from methyl n-propyl aniline and benzyl iodide, was mixed with equimolecular quantity of anhydrous silver salt of dextro bromocamphorsulphonic acid in an acetone ethyl acetate solution, and boiled on a water bath for 2 hours. The filtrate separated from silver iodide was subjected to distillation to remove the solvent, and the yellow syrupy residue changed to a solid mass on allowing to stand in a desiccator over a night. The crystalline mass consisting of a mixture of dextro and lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate, was dissolved in hot acetone and left in a desiccator.

The crystals melting at 161–162° gave the specific rotatory power $[\alpha]_D^{25} = +51{\cdot}68°$ in an aqueous solution, which corresponds to that of the racemic ammonium dextro-bromocamphorsulphonate.

Then, the whole mass was dissolved in ethyl acetate, and from such a solution lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate isolated in white needle-shaped crystals. The

1 Mem. Coll. Sci. Engin., Kyoto, **3**, 371 (1912).

mother liquor was made to evaporate down to a small bulk, and some ether added in order to promote the further crystallisation. Adding more ether to the filtrate from the second crop of the crystals, we have obtained hygroscopic needle-shaped crystals, and finally a syrupy residue containing dextro methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate. To the syrup dissolved in water, was added a potassium iodide solution in order to precipitate all the sulphonate present as the crystalline iodide, and methyl n-propyl phenyl benzyl ammonium iodide thus formed was allowed to recrystallize from alcohol.

It melts at 148°, and its specific rotatory power in its alcoholic solution was found to be $[\alpha]_D^{25} = +90{\cdot}90°$.

The three fractions of the active bromocamphorsulphonate crystallized out from the ethyl acetate regularly increase their hygroscopic character from the first to the third, also showing the difference in the specific rotatory power in their aqueous solutions, i.e., $[\alpha]_D^{25} = +1{\cdot}48°$, $[\alpha]_D^{25} = -0{\cdot}87$ and $[\alpha]_D^{25} = -2{\cdot}57°$ respectively.

Repeating the recrystallisation of the first fraction several times from ethyl acetate, finally it was found to possess the constant rotatory power $[\alpha]_D^{25} = -2{\cdot}57°$ which agrees with that of the pure lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate. The substance thus obtained was no longer hygroscopic as was observed by Jones,[1] and has no definite melting point. Colourless crystals when heated at 80° for a while became opaque, and the cause of such a phenomena is due to the escape of the ethyl acetate of crystallisation which is contained in the molecule, as was ascertained by the author by the usual method.

The melting points and rotatory powers in the alcoholic solutions of the active ammonium iodide, bromide and chloroplatinate derived from optically active ammonium dextro-bromocamphorsulphonates, have been studied , and the results of the experiments by the author together with those of Wedekind and Fröhlich,[2] will be shown in the table I :

1 J. Chem. Soc., 89, 281 (1906).

2 Zur Stereochemie d. fünfwertigen Stickstoffes, 1907, S. 49.

TABLE I.

	Wedekind & Fröhlich.	Author.
l-$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N\cdot C_{10}H_{14}BrSO_4$	$[\alpha]_D^{25} = -2{\cdot}67°$	$[\alpha]_D^{25} = -2{\cdot}57°$
l-$(CH_3)(C_3H_7)(C_6H_5)C_7H_7)NI$	[119–150°]: $[\alpha]_D = -96{\cdot}47°$	[146–147°]; $[\alpha]_D^{25} = -93{\cdot}63°$
l-$(CH_3)(C_3H_7)C_6H_5)(C_7H_7)NBr$	— —	[166–167°]; $[\alpha]_D^{25} = -124{\cdot}3°$
l-$[(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NCl]_2PtCl_4$	—	[164·5–164°]
d-$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NI$	$[\alpha]_D = +86{\cdot}74°$	$[\alpha]_D^{25} = +90{\cdot}90°$

The author has attempted to resolve *α* methyl allyl phenyl benzyl ammonium iodide prepared from methyl benzyl aniline and allyl iodide, into its optical antipodes by means of silver dextro-bromocamphorsulphonate in an acetone or ethyl acetate solution, and the white platy crystals obtained by the fractional crystallisation of the racemic methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate in the acetone solution, melted at 135–136° and gave the specific rotatory power, $[\alpha]_D^{25} = +51{\cdot}59°$, in an aqueous solution. After a repeated crystallisation from acetone, the rotatory power of the substance was again determined, and observed to be $[\alpha]_D^{25} = +52{\cdot}28°$, and *γ* methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate like the *α* compound, also melted at 135–136° and gave the specific rotatory power, $[\alpha]_D^{25} = +52{\cdot}77°$.

Thus the author's endeavour to resolve methyl allyl phenyl benzyl ammonium iodides (both *α* and *γ* forms) by means of bromocamphorsulphonic acid, into optically active compounds has not been succeeded.

The author, therefore, used Pope and Peachey's[1] method, and fortunately succeeded in resolving both ammonium iodides into their optically active forms.

Pure *α* methyl allyl phenyl benzyl ammonium iodide and anhydrous silver dextro-camphorsulphonate mixed in equimolecular quantities in an acetone ethyl acetate solution, was heated over a water bath for 1½ hours. After separating silver iodide, the solution was subjected to distillation, and the residue consisting of a viscid liquid, when

1 J. Chem. Soc., **75**, 1127 (1899); **79**, 828 (1901).

was allowed to stand over sulphuric acid in a dark and cold place for a week, deposited crystals. By repeating fractional crystallisation from acetone six times, there were obtained white needle-shaped crystals melting at 161–162°, which gave the mean specific rotatory power of $[\alpha]_D^{25} = +46{\cdot}48°$ in an aqueous solution. From the mother liquor, crude lævo *α* methyl allyl phenyl benzyl ammonium iodide was isolated by the aid of a potassium iodide solution, which was utilized for the preparation of the pure lævo isomeride.

In the winter time when the author repeated the same experiment, the yield of the crystalline mass consisting of a mixture of dextro and lævo methyl allyl phenyl benzyl ammonium dextro-camphorsulphonates was more fruitful, owing to the influence of the external conditions—temperature and humidity of the atomosphere. In the fractional crystallisation of the racemic camphorsulphonates, ethyl acetate was used as a solvent according to Pope and Harvey.[1]

The first crop of the crystals consisted of almost pure dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate which when recrystallized from ethyl acetate 5 times and then from acetone twice, formed white needle-shaped crystals melting at 162–163°, whose specific rotatory power in an aqueous solution was found to be $[\alpha]_D^{25} = +46{\cdot}71°$ as the mean value. The second crop consisted of white needle-shaped crystals, and the third hygroscopic rhombic crystals, and their rotatory powers, determined in aqueous solutions, were observed to be $[\alpha]_D^{25} = +38{\cdot}27°$ and $[\alpha]_D^{25} = -1{\cdot}28°$ respectively.

The crude lævo ammonium iodide separated from the mother liquor from the last crop was treated with an equimolecular silver lævo-camphorsulphonate. Carrying out the process of the crystallisation of the reaction product as described in its optical antipode, pure lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was obtained in white needle-shaped crystals melting at 160–161° which in an aqueous solution gave the mean specific rotatory power of $[\alpha]_D^{25} = -46{\cdot}49$.

In another experiment, pure lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was prepared from the externally compensated ammonium iodide and silver lævo-camphorsulphonate; it consisted of white needles which were found to have the melting point 162–163° and the specific rotatory power, $[\alpha]_D^{25} = -46{\cdot}69°$.

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1 *Loc. cit.*

Now, the author, expecting that stereoisomers may exist in the active forms of the ammonium compound, has undertaken the resolution of γ methyl allyl phenyl benzyl ammonium iodide by means of anhydrous silver dextro-camphorsulphonate, and γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained and recrystallized from acetone, consisted of white needles which melt at 162°, and its mean specific rotatory power in an aqueous solution was found to be $[\alpha]_D^{25} = +58{\cdot}46°$.

Since the specific rotatory power of the γ form is not altered by recrystallisation, it is noteworthy that the pure sample of α methyl allyl phenyl benzyl ammonium compound has lower specific rotatory power than that of the γ isomer.

Now, the author has to ascribe the difference of the specific rotatory powers in α and γ isomerides to the different configurations of the atomic groups in their molecules.

For the confirmation of this view, the author has conducted the experiment to be described below:

In the experiment, the racemic dextro-camphorsulphonate was macerated with ethyl acetate according to Pope and Harvey,[1] and the purified γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate used had the properties already stated, i.e., the white needle-shaped crystals melted at 163°, and the specific rotatory power of the well purified sample in an aqueous solution was found to be $[\alpha]_D^{25} = +58{\cdot}76°$ as the mean value.

To the crude γ lævo methyl allyl phenyl benzyl ammonium iodide obtained from the impure dextro methyl allyl phenyl benzyl ammonium dextro camphorsulphonate, an equimolecular silver dextro-camphorsulphonate was added, and the reaction product was subjected to fractional crystallisation using acetone as the solvent. And pure γ lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate, thus obtained, was found to be white needle-shaped crystals which had the properties similar to those of the enantiomorphous compound; it melted at 163–164° and its specific rotatory power was shown to be $[\alpha]_D^{25} = -56{\cdot}21°$, which is lower than that of its enantiomorph.

γ lævo methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate prepared from racemic γ methyl allyl phenyl benzyl ammonium iodide and silver lævo-camphorsulphonate was observed to have the same

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1 *Loc. cit.*

melting point, the same specific rotatory power and the same crystalline form as those of the compound above mentioned.

The author has prepared several other optically active ammonium compounds of the α and γ series; and compared their melting point, specific rotatory power in alcohol or chloroform solutions with those of the same substances stated by Pope and Harvey,[1] as shown in the table II.

TABLE II.

α Compounds.	Pope and Harvey.	Author.
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}C_{10}H_{15}SO_4$	$[171-173°]$ $[\alpha]_D^{14}=+46{\cdot}6°$	$[162-163°]$ $[\alpha]_D^{25}=+46{\cdot}71°$
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I$	$[147°]$ $[\alpha]_D^{17}=+55{\cdot}4°$	$[135-136°]$ $[\alpha]_D^{25}=+68{\cdot}28°$ [2] $[\alpha]_D^{25}=+51{\cdot}72°$ [3]
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}Br$	$[165-167°]$ $[\alpha]_D^{16.2}=+64{\cdot}1°$ (chloroform)	$[155-156°]$ $[\alpha]_D^{25}=+67{\cdot}44°$ (alcohol)
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI,HgI_2$	$[124-125°]$ $[\alpha]_D^{11}=+24{\cdot}3°$	$[119-120°]$ $[\alpha]_D^{25}=+24{\cdot}86°$
d-$[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NCl]_2PtCl_4$	$[166°]$	$[149-150°]$
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}C_{10}H_{14}SO_4$	$[171-173°]$ $[\alpha]_D^{19}=-45{\cdot}5°$	$[162-163°]$ $[\alpha]_D^{25}=-46{\cdot}59°$
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI$	$147°$ $[\alpha]_D^{17}=-53{\cdot}4°$ (chloroform)	$[134-135°]$ $[\alpha]_D^{25}=-51{\cdot}34°$ (alcohol)
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI,HgI_2$	$[125-126°]$ $[\alpha]_D^{14.5}=-23{\cdot}5°$	$[119-120°]$ $[\alpha]_D^{25}=-24{\cdot}12°$

1 *Loc. cit.*
2 In chloroform.
3 In alcohol.

γ-Compounds.	Author.	
	Melting point.	$[\alpha]_D^{25}$
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}S_{10}H_{15}SO_4$	[163°]	+58·61°
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I$	[134–135°]	+73·98°[1] / +65·54°[2]
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}Br$	[155–156°]	+81·80°
d-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I,HgI_2$	[120–121°]	+39·51°
d-$[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}Cl]_2PtCl_4$	[148–149°]	
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}C_{10}H_{15}SO_4$	[163–165°]	−56·21°
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I$	[135–135,5°]	−63·15°
l-$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I,HgI_2$	[120°]	−39·60°

From the experimental results so far obtained the following conclusions are drawn:

1. The asymmetrical ammonium compounds prepared by the author, may directly resolve into optically active antipodes by means of optically active acids.

2. Whilst the melting points of the same optically active compounds obtained by the same method, do not agree with those of the other investigators, their specific rotatory powers are concordant to each other.

3. In the optically active methyl allyl phenyl benzyl ammonium compounds, there exist optical isomers in α and γ forms, which possess the same melting points but the different specific rotatory powers.

The optically active acids used for the resolution were dextro-camphorsulphonic, lævo-camphorsulphonic and dextro-bromocamphorsulphonic acids. And dextro-camphorsulphonic acid was prepared according to Reychler[3] from Japan camphor purified by sublimation and by treating with conc. sulphuric acid and acetic anhydride, and it was obtained in the form of hygroscopic crystals melting at 192–193°, showing its specific rotatory power as $[\alpha]_D^{25} = +23{\cdot}14°$ in its aqueous solution. Lævo-

[1] In chloroform.

[2] In alcohol.

[3] Bull. Soc. Chim., **19**, 120 (1898).

camphorsulphonic acid used in the experiment was prepared according to Pope and Harvey[1] from lævo-borneol from Kahlbaum, and its melting point was found to be 190° and the specific rotatory power of its ammoninm salt in the aqueous solution to be $[\alpha]_D^{25} = -21{\cdot}35°$. Dextro-bromocamphorsulphonic acid obtained according to the method suggested by Morsh and Cousins,[2] from dextro-bromocamphor crystallized from methyl alcohol and chlorosulphonic acid, was purified by converting it into the ammonium salt which possessed the specific rotatory power, $[\alpha]_D^{25} = +85{\cdot}54°$, in an aqueous solution.

EXPERIMENTAL PART.

1. *Dextro-Camphorsulphonic Acid,* $C_{10}H_{15}O{\cdot}SO_3H$.

The substance was prepared by Reychler's method,[3] and the process will be mentioned below:

152 parts Japan camphor purified by sublimation were treated with the mixture of 204 parts acetic anhydride from Merck and 98 parts pure conc. sulphuric acid. After a while dextro-camphorsulphonic acid crystallized out in needles, which were separated from the mother liquor by filtration, washed with ether and then recrystallized from acetic acid. The substance dried at 100° for 3 hours and observed to melt at 192–193°, was analysed and gave the following results:

0·1953 grm. substance gave 0·1916 grm. $BaSO_4$.

	Calc. for $C_{10}H_{16}O_4S$.	Found.
Sulphur	13·79	13·46

The optical rotation of the free acid in an aqueous solution was determined:

A solution of 0·8751 grm. acid made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}62°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +23{\cdot}14°$.

2. *Lævo-Camphorsulphonic Acid,* $C_{10}H_{15}O{\cdot}SO_3H$

l-Camphor prepared according to Pope and Harvey[4] from l-borneol from Kahlbaum by oxidation with nitric acid (sp. gr. 1·42) was converted into lævo-camphorsulphonic acid by the usual way.

1 J. Chem. Soc., **79**, 76, 80 (1901).
2 J. Chem. Soc., **59**, 966 (1891).
3 Bull. Soc. Chim.; [III], **19**, 120 (1898).
4 J. Chem. Soc., **79**, 76 (1901).

The acid purified by crystallisation from acetic acid was found to melt at 190°. Converting it into the ammonium salt, its analysis and optical determination were carried on, with the following results :

0·4098 grm. substance gave 0·3896 grm. $BaSO_4$.

	Calc. for $C_{10}H_{19}O_4SN$.	Found.
Sulphur	13·61	13·06

A solution of 0·3981 grm. of the ammonium salt made up to 25 c.c. with water at 25° gave $\alpha_D^{25} = -0·68°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -21·35°$. Pope and Harvey gave for its value $[\alpha]_D = -20·7°$.

3. *Dextro-Bromocamphorsulphonic Acid and its Salts.*

The following experiments were conducted according to the method suggested by Marsh and Cousins.[1] To prepare the acid, 100 grms. dextro-bromocamphor purified by recrystallisation from methylated alcoholic solution and dissolved in 200 grms. pure dried chloroform were mixed with 75 grms. of fresh distilled chlorosulphonic acid prepared after Muller,[2] and the whole contents of a vessel were heated over a water bath for 15 hours. The brown solution was then poured into cold water, and the chloroform separated from the brownish-yellow aqueous part. The acidic aqueous solution was neutralized with calcium carbonate; removeing calcium sulphate by filtration, a brownish-yellow solution containing crude calcium bromocamphorsulphonate was obtained. The calcium salt was converted into the ammonium salt which crystallized out from hot water in white needle-shaped crystals.

The analysis of the pure ammonium salt gave the following value for sulphur :

0·1996 grm. substance gave 0·1274 grm. $BaSO_4$.

	Calc. for $C_{10}H_{18}O_4NSBr$.	Found.
Sulphur	9·76	9·74

A solution of 1·27 grm. of the ammonium salt made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +8·69°$ in a 20 cm. tube, whence $[\alpha]_D^{25} = +85·54°$ and $[M]_D^{25} = +280·59°$, while Marsh and Cousins[3] gave $[\alpha]_D^{25} = +87·52°$ and Kipping and Pope[4] $[\alpha]_D^{25} = +84·78°$ for its specific rotation in the aqueous solution.

1 J. Chem. Soc., **59**, 970 (1891).
2 Ber. D. Chem. Ges., **6**, 227 (1878).
3 J. Chem. Soc., **59**, 966 (1891).
4 *Ibid.*, **67**, 354 (1895).

Starting from the ammonium salt the author has prepared the barium salt, free acid and silver salt successively, and used the silver salt for the resolution of the asymmetric ammonium iodide.

4. Resolution of Methyl n-Propyl Phenyl Benzyl Ammonium Iodide into its Optically Active Components.

A. Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Dextro-Bromocamphorsulphonate,

$$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N\cdot O\cdot SO_2\cdot C_{10}H_{14}BrO, CH_3\cdot CO_2\cdot C_2H_5.$$

One molecule of methyl n-propyl phenyl benzyl ammonium iodide prepared from methyl n-propyl aniline and benzyl iodide, was mixed with one molecule of anhydrous silver dextro-bromocamphorsulphonate, and boiled in a mixture of acetone and ethyl acetate for 2 hours over a water bath. After the reaction has been completed, the silver iodide was separated, the solvent distilled off and a brown syrupy residue allowed to stand, solidifing in a crystalline mass. The crystalline mass, thus formed, was dissolved in acetone, from which white crystals were obtained. The crystals purified by recrystallisation from acetone, melted at 141–142° and were analysed:

0·235 grm. of the substance gave 0·1028 grm. $BaSO_4$.

	Calc. for $C_{27}H_{36}O_4NSBr$.	Found.
Sulphur	5·81	6·01

The rotatory power of the pure preparations a and b was determined in the aqueous solutions with the following results:

a). A solution of 0·866 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +3{\cdot}50°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51{\cdot}68°$ and $[M]_D^{25} = +284{\cdot}2°$.

b). A solution of 0·7021 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +3{\cdot}15°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +56{\cdot}26°$.

From the analytical results and polarimetric measurements above stated, it is quite evident that the substance would be the racemic one from which racemic methyl n-propyl phenyl benzyl ammonium iodide has been derived as will be shown in the follewing polarimetric experiment:

A solution of 0·1084 grm. of the iodide made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}02°$ in a 20 cm. tube, whence $[\alpha]_D^{25} = +1{\cdot}4°$.

By the fractional crystallisation of the racemic bromocamphorsulphonate in ethyl acetate, lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate separated out in white needle-shaped crystals, and the mother liquor, on evaporation, yielded platy crystals; adding ether to the second filtrate, the third crop in the hygroscopic crystals and finally a syrupy residue were obteined. To the latter dissolved in water, was added an excess of a potassium iodide solution to precipitate the base as iodide.

The rotatory power of the crystallized fractions above mentioned, were determined in their aqueous solutions, and the results will be shown as follows:

1. *The first fraction*, recrystallized from ethyl acetate three times:

A solution of 1·1807 grm. substance made up to 25 c.c. with water at 25°, gave $[\alpha]_D^{25} = -0{\cdot}14°$ in a 20 cm. tube, whence $[\alpha]_D^{25} = -1{\cdot}48°$.

2. *The second fraction:*

A solulion of 0·5738 grm. of the substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = -0{\cdot}04$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -0{\cdot}09°$.

3. *The third fraction:*

A solution of 0·7836 grm. of the substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0{\cdot}15$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +2{\cdot}07°$.

In order to fix the optical rotation constant, the first crop was recrystallized several times from ethyl acetate, and the rotatory powers of the purified different preparations were determined in aqueous solutions and the results will be seen in the following statements:

a). A solution of 0·8157 grm. of the substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = -0{\cdot}16°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -2{\cdot}45°$.

b). A solution of 0·6316 grm. of the substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = -0{\cdot}13°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -2{\cdot}57°$.

Pure lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate has the mean specific rotatory power $[\alpha]_D^{25} = -2{\cdot}51°$ in an aqueous solution, but no definite melting point; it was soluble in acetone, ethyl acetate, alcohol and water but not in ether.

Since the crystals when heated at 80° became opaque, the author was led to the suspicion that they might contain solvent in the molecule.

When 1·419 grm. of the pure crystals obtained from the ethyl acetate solution, were heated in an air bath at 80° for 5 hours, it was observed that the loss of weight amounted to 0·1821 grm. which just correspond to the calculated value of ethyl acetate of crystallisation (1 mole.) for one molecule of the active substance.

	Calc. for $C_{29}H_{36}O_4NSBr.CH_3CO_2C_2H_5$.	Found.
Ethyl acetate	13·79	12·83

The substance gave the following analytical result :

0·27 grm. the substance gave 0·0385 grm. $BaSO_4$.

	Calc. for $C_{31}H_{42}O_6NSBr$.	Found.
Sulphur	5·02	5.02

B. Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Iodide,

$$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NI.$$

Adding a potassium iodide solution to an aqueous solution of pure dextro methyl n-propyl phenyl benzyl ammonium dextro-bromocamphor-sulphonate, white crystalline precipitate of lævo methyl n-propyl phenyl benzyl ammonium iodide soon began to separate out; it was recrystallized from hot alcohol in a dark place with the protection of optical inversion by the sun light. The platy crystals, thus obtained, were soluble in alcohol and acetone, and most easily in chloroform, and melted at 146–147°.

The analysis and determination of the rotatory power of the substance were made, and the results will be shown as follows;

0·2481 grm. of ths substance gave 0·1592 grm. AgI.

	Calc. for $C_{17}H_{22}NI$.	Found.
Iodine	34·62	34·68

a). A solution of 0·991 grm. iodide made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0·68°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -93·31°$.

b). A solution of 0·1028 grm. iodide made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0·77°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -93·63°$.

c). A solution of 0·1016 grm. iodide made up to 25 c.c. with

alcohol at 25°, gave $\alpha_D^{25} = -0{\cdot}76°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -93{\cdot}51°$.

Consequently the mean specific rotatory power of the iodide is $[\alpha]_D^{25} = -93{\cdot}48°$.

C. Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Bromide,

$$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)NBr.$$

The substance prepared from pure dextro methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate and potassium iodide, crystallized in rhombic prisms from alcoholic solution. It melts at 166–167° and is more soluble in organic solvents than the corresponding iodide.

The analytical result of the substance will be mentioned below:

0·2244 grm. substance gave 0·1317 grm. AgBr.

	Calc. for $C_{17}H_{22}NBr$.	Found.
Bromine	25·00	24·98

The determination of the rotatory power was conducted with the purified substance, and the result is as follows:

A solution of 0·116 grm. bromide made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{22} = -1{\cdot}06°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -114{\cdot}2°$.

D. Lævo Methyl n-Propyl Phenyl Benzyl Ammonium Chloroplatinate,

$$[(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N{\cdot}Cl]_2Pt{\cdot}Cl_4.$$

Lævo methyl n-propyl phenyl benzyl ammonium hydroxide obtained by the interaction of pure lævo methyl n-propyl phenyl benzyl ammonium iodide and moist silver oxide, was neutralized with hydrochloric acid; the ammonium chloride thus formed was converted into the double salt with platinic chloride.

The double salt recrystallized from a large quantity of hot water, was yellow fine needle-shaped crystals, melting at 163·5–164°, while the corresponding inactive salt melts at 159–160°.

The salt, dried at 100°, was analysed and gave the following result:

0·1824 grm. double salt gave 0·039 grm. Pt on ignition.

	Calc. for $C_{34}H_{44}N_2Cl_6Pt$.	Found.
Platinum	22·01	21·49

E. Dextro Methyl n-Propyl Phenyl Benzyl Ammonium Iodide,

$(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N{\cdot}I$.

Evaporating the filtrate from lævo methyl n-propyl phenyl benzyl ammonium dextro-bromocamphorsulphonate, there was left a syrupy residue from which dextro methyl n-propyl phenyl benzyl ammonium iodide was obtained in white crystalline form. It crystallizes from alcohol in white plates which melt at 146–147° as observed in its antipode.

The analysis of the substance gave the following result :

0·3449 grm. substance gave 0·2182 grm. AgI.

	Calc. for $C_{17}H_{22}NI$.	Found.
Iodine	34·62	34·19

a). A solution of 0·098 grm. iodide made up to 25c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}70°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +89{\cdot}28°$.

b). A solution of 0·0977 grm. iodide recrystallized from alcohol, made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}71$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +90{\cdot}84°$.

F. Dextro Methyl n-Propyl Phenyl Benzyl Ammonium Chloroplatinate,

$[(CH_3)(C_3H_7)(C_6H_5)(C_7H_7)N{\cdot}Cl]_2{\cdot}PtCl_4$.

The double salt with platinic chloride prepared from dextro methyl n-propyl phenyl benzyl ammonium iodide by the usual method, consists of yellow fine needle-shaped crystals which melt at 163–164°. Its analysis gave the following result :

0·1906 grm. of the double salt gave 0·0416 grm. Pt on ignition.

	Calc. for $C_{34}H_{44}N_2Cl_6Pt$.	Found.
Platinum	22·01	21·84

5. Resolution of Methyl Allyl Phenyl Benzyl Ammonium Iodide into its Optically Active Components.

A. α Methyl Allyl Phenyl Benzyl Ammonium Dextro-Bromocamphorsulphonate,

$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}O{\cdot}SO_2C_{10}H_{14}BrO$.

α Methyl allyl phenyl benzyl ammonium iodide prepared from methyl benzyl aniline and allyl iodide, was boiled with an equi-

molecular silver dextro-bromocamphorsulphonate in an acetone-ethyl acetate solution on a water bath for 2 hours.

By the recrystallisation of the reaction product three times from acetone, α methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate was obtained in white plates which melt at 133–134°.

It is soluble in acetone, ethyl acetate, alcohol and water, dried at 100° it was analysed:

0·2054 grm. substance gave 0·082 grm. $BaSO_4$.

	Calc. for $C_{27}H_{34}O_4NSBr$.	Found.
Sulphur	5·84	5·48

a). A solution of 0·94 grm. of the substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +3{\cdot}86°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51{\cdot}33°$.

b). A solution of 0·8142 grm. of the substance recrystallized from acetone, made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +3{\cdot}36°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51{\cdot}56°$.

c). A solution of 0·3493 grm. of the substance (the sample b recrystallized three times from ethyl acetate) made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}37°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +49{\cdot}63°$.

d). A solution of 0·263 grm. of the substance (the sample c recrystallized 4 times from ethyl acetate) made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}10°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +52{\cdot}28°$.

The ammonium iodide derived from the ammonium bromocamphorsulphonate was observed to be optically inactive.

B. γ Methyl Allyl Phenyl Benzyl Ammonium Dextro-Bromocamphorsulphonate,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_{14}BrO.$$

By the interaction of γ methyl allyl phenyl benzyl ammonium iodide, prepared from methyl allyl aniline and benzyl iodide, and silver dextro-bromocamphorsulphonate, γ methyl allyl phenyl benzyl ammonium dextro-bromocamphorsulphonate was obtained, which crystallizes in white crystals from acetone. It melts at 135–136°, and its analysis gave the following result.

0·2251 grm. of the substance gave 0·0941 grm. $BaSO_4$.

	Calc. for $C_{27}H_{34}O4NSBr$.	Found.
Sulphur	5·84	5·74

The optical measurement of 2 preparations, a and b was conducted, and the results are as follows:

a). A solution of 1·0086 grm. of the substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +4{\cdot}01°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +50{\cdot}81°$.

b). A solution of 0·7699 grm. of the substance obtained by the crystallisation of the preparation a, made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} + = 3{\cdot}25°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +52{\cdot}77°$.

C. α Dextro Methyl Allyl Phenyl Benzyl Ammonium Dextro-Camphorsulphonate,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}O{\cdot}SO_2C_{10}H_{15}O.$$

In June, the author attempted the resolution of α methyl allyl phenyl benzyl ammonium iodide by means of dextro-camphorsulphonate[1], and on standing the acetone solution of the reaction product in a desiccater, kept in a dark and cold place for a week, the crystals began to separate out from the solution, but its yield was very poor. The substance recrystallized five times from acetone consisted of colourless needles which were found to melt at 161–162°. They are soluble in water, acetone, ethyl acetate and alcohol; their analysis gave the following result:

0·178 grm. substance gave 0·0878 grm. $BaSO_4$.

	Calc. for $C_{27}H_{33}O_4NS$.	Found.
Sulphur	6·82	6·78

The rotatory power of the substance was determined in an aqueous solution, with the following results:

a). A solution of 0·8525 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +3{\cdot}17°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +46{\cdot}48°$.

b). A solution of 0·5327 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +2{\cdot}02°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +47{\cdot}40°$.

Adding potassium iodide to the mother liquor separated from dextro methyl allyl phenyl benzyl ammonium d-camphorsulphonate, lævo methyl allyl phenyl benzyl ammonium iodide was obtained in an impure state;

[1] Pope and Harvey, J. Chem. Soc. **75**, 1127 (1899).

the substance recrystallized from ethyl alcohol was found to melt at 127–128° and the specific rotatory power to be $[\alpha]_D^{25} = -29{\cdot}33°$ in alcoholic solution.

In the second experiment performed in winter, the yield of racemic methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate was more fruitful than in the previous experiment ; it was macerated with ethyl acetate according to Pope and Harvey[1].

The first crop consisted of colourless needles ; after evaporating the mother liquor to a small bulk, and then on standing it over sulphuric acid, we get the second crop.

From the mother liquor of the second crop, rhombic crystals deposited as the third crop. Evaporating the residual liquor almost to dryness, and then adding a large quantity of ether, hygroscopic crystals were formed, and finally the syrupy residue was dissolved in water and converted into the iodide.

For each fraction the optical measurement was made in its aqueous solution and the results will be mentioned below :

The first fraction :

The crystals obtained by recrystallizing from ethyl acetate 5 times melted at 162°, and the optical rotation for each of 4 pure preparations a, b, c and d was determined.

a). A solution of 0·2082 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0{\cdot}77°$ in a 20 cm. tube ; whence $[\alpha]_D^{25} = +46{\cdot}23°$.

b). A solution of 0·1423 grm. substance obtained by the recrystallisation twice from acetone, made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0{\cdot}54°$ in a 20 cm. tube ; whence $[\alpha]_D^{25} = +47{\cdot}43°$.

c). A solution of 0·3132 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}17°$ in a 20 cm. tube ; whence $[\alpha]_D^{25} = +46{\cdot}67°$.

d). A solution of 0·3176 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{26} = +1{\cdot}20°$ in a 20 cm. tube ; whence $[\alpha]_D^{25} = +47{\cdot}23°$.

The mean value is, therefore, $[\alpha]_D^{26} = +46{\cdot}91°$, while Jone[2] in one hand and Pope and Harvey[3] on the other gave $[\alpha]_D = +46{\cdot}8$ and $[\alpha]^D = +46{\cdot}6°$ respectively.

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1 *Loc. cit.*

2 *Loc. cit.*

3 *Loc. cit.*

The second fraction :

A solution of 0·3168 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0{\cdot}97°$ in a 20 cm. tube ; whence $[\alpha]_D^{25} = +38{\cdot}27°$.

The third fraction :

A solution of 0·1983 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = 0$ in a 20 cm. tube.

The fourth fraction :

A solution of 0·2382 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = -0{\cdot}07°$ in a 20 cm. tube ; whence $[\alpha]_D^{25} = -1{\cdot}32°$.

D. γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Dextro Camphorsulphonate,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_{15}O.$$

A. Equimolecular mixture of γ methyl allyl phenyl benzyl ammonium iodide and silver dextro-camphorsulphonate was heated in a acetone-ethyl acetate solution for 2½ hours on a water bath. From the reaction product, dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate was obtained in the like manner as was described in the case of the α compound, the substance crystallizing from acetone in white needles and melting at 162°.

It is soluble in alcohol, acetone, ethyl acetate and water but not in ether. The sulphur contents and the rotatory power of the substance were determined with the following results :

0·2101 grm. of the substance gave 0·1043 grm. $BaSO_4$.

	Calc. for $C_{27}H_{35}O_4NS$.	Found.
Sulphur	6·82	6·82

a). A solution of 0·8444 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +3{\cdot}87°$ in a 20 cm. tube ; whence $[\alpha]_D^{25} = +57{\cdot}29°$.

b). A solution of 0·9161 grm. the substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +4{\cdot}37°$ in a 20 cm. tube ; whence $[\alpha]_D^{25} = +59{\cdot}63°$. The mean value of the rotatory power is, therefore, accounted for as $[\alpha]_D^{25} = +58{\cdot}46°$.

The filtrate from the crystals of dextro ammonium dextro-camphorsulphonate was dissolved in water, and then potassium iodide solution added to transform the base contained in it into the iodide whose rotatory power in an alcoholic solution has been observed to be $[\alpha]_D^{25} = -25{\cdot}0°$.

B. As the second experiment, the racemic dextro-camphorsulphonate was subjected to the fractional crystallisation in ethyl acetate, and the pure γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained, consisted of white needles which melt at 163–164°. The determination of the rotatory power of the substance was conducted with the purified different preparations a, b and c in their aqueous solutions.

a). A solution of 0·2532 grm. substance made up to 25 c.c with water at 25°, gave $\alpha_D^{25} = +1{\cdot}20°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +59{\cdot}24°$.

b). A solution of 0·2342 grm. substance obtained by the recrystallisation of the preparation a) from acetone, made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}10°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +58{\cdot}71°$.

c). A solution of 0·3572 grm. of the same preparation as used in b) made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}67°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +58{\cdot}44°$.

The mean value of the specific rotatory power is, therefore, accounted for as $[\alpha]_D^{25} = +58{\cdot}66°$.

E. α Lævo Methyl Allyl Phenyl Benzyl Ammonium Lævo Camphorsulphonate,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_{15}O.$$

A. By the interaction of 5 grm. raw α lævo methyl allyl phenyl benzyl ammonium iodide and 5 grm. silver lævo-camphorsulphonate, 2·5 grm. lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was obtained in pure state.

The substance recrystallized from acetone three times, melts at 160–161°, and has the same chemical and physical properties as its enantiomorphous salt. The specific rotatory power in its aqueous solution was determined to be opposite in its sign to that of its antipode but with the same magnitude as will be shown in the following statements:

a). A solution of 0·3069 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = -1{\cdot}14°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -46{\cdot}43°$.

b). A solution of 0·2927 grm. substance made up to 25 c.c. with

water at 25°, gave $\alpha_D^{25} = -1{\cdot}09°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -46{\cdot}55°$.

The analytiscal result is as follows:

0·3097 grm. of the substance gave 0·1533 grm. $BaSO_4$,

	Calc. for $C_{27}H_{35}O_4NS$.	Found.
Sulphur	6·82	6·80

B. The substance, also, prepared from 6 grm. *α* methyl allyl phenyl benzyl ammonium iodide and 6 grm. silver lævo camphorsulphonate in an acetone-ethyl acetate solution, and its yield in pure state was found to be about 1 grm.

The pure preparation melting at 162–163° gave the following value of the optical rotatory power in an aqueous solution.

A solution of 0·2249 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = -0{\cdot}84°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -46{\cdot}69°$.

F. γ Lævo Methyl Allyl Phenyl Benzyl Ammonium Lævo-Camphorsulphonate.

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_{15}O.$$

A. 4 grm. crude γ l methyl allyl phenyl benzyl ammonium iodide (its specific rotatory power in alcohol solution being $[\alpha]_D^{25} = -25{\cdot}0°$) was made to react with 4 grm. silver l-camphorsulphonate in an acetone-ethyl acetate solution, and 1 grm. pure γ l methyl allyl phenyl benzyl ammonium l-camphorsulphonate was obtained. It crystallizes from acetone in white needle-shaped crystals which melt at 163–164°, possessing all the other same chemical and physical properties as those of its antipode.

0·357 grm. of ths substance, gave 0·1792 grm. $BaSO_4$ by analysis.

	Calc. for $C_{27}H_{35}O_4NS$.	Found.
Sulpdur	6.82	6.89

A solution of 0·2581 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = -1{\cdot}09°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -55{\cdot}70°$.

A solation of 0·2422 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = -1{\cdot}09°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -56{\cdot}21°$.

B. Pure γ lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate was also prepared by the interaction of 6·5 grm. γ racemic methyl allyl phenyl benzyl ammonium iodide and 6 grm. silver lævo camphorsulphonate, and its yield was found to be about 1·5 grm.

The melting point of the substance was observed to be 162–163° and its specific rotatory power was determined in an aqueous solution.

A solution of 0·2244 grm. substance made up to 25 c.c. with water at 25°C, gave $\alpha_D^{25} = -1{\cdot}02°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -56{\cdot}82°$.

G. α Dextro Methyl Allyl Phenyl Benzyl Ammonium Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I.$$

A. By adding potassium iodide to an aqueous solution of pure α dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate prepared in the first experiment, α dextro methyl allyl phenyl benzyl ammonium iodide precipitated as a white crystalline powder, which was separated from the mother liquor and recrystallized from an alcoholic solution in a dark place.

The white needle-shaped crystals melt at 135–136° with some decomposition and were found to have the same chemical properties with its inactive isomer.

A solution of 0·1211 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}50°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51{\cdot}61°$.

B. The pure active iodide also prepared from the active ammonium dextro-camphorsulphonate obtained in the second experiment, consists of white needles melting at 135–136°.

The specific rotatory powers of the two preparations were determined in the alcohol and chloroform solutions with the following results:

a). A solution of 0·1254 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}52°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51{\cdot}84°$.

b). A solution of 0·2102 grm. substance made up to 25 c.c. with chloroform at 25°, gave $\alpha_D^{25} = +0{\cdot}92°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +58{\cdot}28°$.

Its analysis gave the result recorded below:

0·22 grm. substance gave 0·1398 grm. AgI.

	Calc. for $C_{17}H_{20}NI$.	Found.
Iodine	34·79	34·34

H. γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I.$$

A. The substance was prepared by the action of potassium iodide upon pure γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate obtained in the first experiment, and that crystallized from alcohol in a dark place, has the same melting point (134–135°), crystalline form and chemical properties as those of the α compound.

The specific rotatory power of the substance was determined in an alcohol solution.

A solution of 0·1254 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}64°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +63{\cdot}64°$.

B. The active iodide obtained from the corresponding active ammonium dextro-camphorsulphonate prepared in the second experiment, melts at 135–136° in a capilary tube.

Its analysis and polarimetric measurement gave the following results:

0·2235 grm. substance gave 0·1438 grm. AgI.

	Calc. for $C_{17}H_{20}NI$.	Found.
Iodine	34·79	34·68

A solution of 0·1281 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}65°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +63{\cdot}45°$.

A solution of 0·2112 grm. substance made up to 25 c.c. with chloroform at 25°, gave $\alpha_D^{25} = +1{\cdot}25°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +73{\cdot}98°$.

It is noteworthy that the iodide of γ form has a higher specific rotatory power than that of α form just as γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate has a higher value than the corresponding α compound.

I. α Lævo Methyl Allyl Phenyl Benzyl Ammonium Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I.$$

The substance formed by the interaction of potassium iodide and pure α lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate, crystallizes in white plates from alcohol in a dark place.

It melts at 134–135° and its chemical properties are same as those of its antipode.

A solution of 0·1047 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0{\cdot}43°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -51{\cdot}34°$.

J. γ Lævo Methyl Allyl Phenyl Benzyl Ammonium Iodide,

$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I$,

The iodide prepared from the corresponding pure γ lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate, crystallizes in white plates melting at 135–135·5°, and all other properties are same as those of the α isomer.

A solution of 0·1062 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0{\cdot}54°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -63{\cdot}14°$.

K. α Dextro Methyl Allyl Phenyl Benzyl Ammonium Bromide,

$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}Br$.

By the action of potassium bromide upon pure α dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, α dextro methyl allyl phenyl benzyl ammonium bromide was obtained, which crystallizes in colourless rhombic prisms from aqueous alcohol in a dark place, and melts at 155–156°. It is more soluble in organic solvents than the corresponding iodide.

0·18 grm. substance gave 0·1054 grm. AgBr.

	Calc. for $O_{17}H_{20}NBr$.	Found.
Bromine	25·15	24·75

A solution of 0·1075 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}57°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +67{\cdot}44°$.

A solution of 0·116 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}63°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +67{\cdot}89°$.

L. γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Bromide,

$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}Br$.

The substance was prepared by the action of potassium bromide upon pure γ dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate.

It crystallizes in colourless rhombic prisms from aqueous alcohol and melts at 155–156°.

It is soluble in alcohol, acetone and chloroform.

The analysis of the substance is as follows:

0·21 grm. substance gave 0·1249 grm. AgBr.

	Calc. for $C_{17}H_{20}NBr$.	Found.
Bromine	25·15	25·31

A solution of 0·136 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0·89°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +81·80°$.

A solution of 0·11 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0·77°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +82·95°$.

M. α Lævo Methyl Allyl Phenyl Benzyl Ammonium Bromide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N·Br.$$

The bromide obtained from α lævo methyl allyl phenyl benzyl ammonium lævo-camphorsulphonate consists of colourless rhombic prisms, and its melting point was found to be 149–150° showing the lower value than that of its antipode. Its optical rotatory power was determined.

A solution of 0·1185 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = -0·60°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -63·29°$.

N. α Dextro Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NI,HgI_2.$$

The substance was prepared by the method of Hope and Harvey[1] by the interaction of equimolecular quantities of pure α dextro methyl allyl phenyl benzyl ammonium iodide and mercuric iodide.

It is soluble in acetone, ethylacetate and alcohol, and crystallizes in yellow plates from ethyl acetate and melts at 119–120°.

A solution of 0·112 grm. substance made up to 25 c.c. with ethyl acetate at 26°, gave $\alpha_D^{25} = +0·22°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +24·56°$.

A solution of 0·1142 grm. substance made up to 24 c.c. with ethyl acetate at 25°, gave $\alpha_D^{25} = +0·23°$ in a 20 cm. tube; whence $\alpha_D^{25} = +25·17°$.

P. γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N·I·HgI_2.$$

[1] *Loc. cit.*

The substance was prepared from γ dextro methyl allyl phenyl benzyl ammonium iodide and mercuric iodide, and crystallizes in yellow plates from ethyl acetate. Its melting point was found to be 120–121°.

A solution of 0·123 grm. substance made up to 25 c.c. with ethyl acetate at 25°, gave $\alpha_D^{25} = +0{\cdot}39°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +39{\cdot}63°$.

A solution of 0·1006 grm. substance made up to 25 c.c. with ethyl acetate at 25°, gave $\alpha_D^{25} = +0{\cdot}32°$ in a 20 cm. tube; whence $[\alpha]_D^{15} = +39{\cdot}39°$.

Q. α Lævo Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I{\cdot}HgI_2.$$

The substance prepared from the corresponding iodide by the usual method consists of yellow plates. It is soluble in alcohol and ethyl acetate, and melts at 119–120°.

A solution of 0·114 grm. substance made up to 25 c.c. with ethyl acetate at 25°, gave $\alpha_D^{24} = -0{\cdot}22°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -24{\cdot}12°$.

R. γ Lævo Methyl Allyl Phenyl Benzyl Ammonium Mercuric Iodide,

$$(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)N{\cdot}I{\cdot}HgI_2.$$

The substance prepared by the action of mercuric iodide upon the corresponding lævo iodide, crystallizes in yellow plates from ethyl acetate and melts at 120°.

A solution of 0·1219 grm. substance made up to 25 c.c. with ethyl acetate at 25°, gave $\alpha_D^{25} = -0{\cdot}39°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = -39{\cdot}99°$.

S. α Dextro Methyl Allyl Phenyl Benzyl Ammonium Chloroplatinate,

$$[(CH_3)(C_3H_5)(C_6H_5)(C_7H_7)NCl]_2, PtCl_4.$$

The chloride obtained by treating the aqueous solution of pure α dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate with sodium chloride solution, was converted into its platinum double salt by the usual method. It crystallizes in yellow fine needles from hot aqueous solution, and melts at 149–150°.

The substance dried at 100° was analysed.

0·2526 grm. double salt gave 0·0565 grm. Pt on ignition.

	Calc. for $C_{34}H_{40}N_2Cl_6Pt$.	Found.
Platinum	22·08	22·40

T. γ Dextro Methyl Allyl Phenyl Benzyl Ammonium Chloroplatinate, $[(CH_3)(C_3M_5)(C_6H_5)(C_7H_7)N\cdot Cl]_2PtCl_4$.

The substanee was prepared from the chloride formed from γ dextro methyl allyl phenyl benzyl ammonium dextro camphorsulphonate, and crystallizes in yellow fine needles from hot aqueous solution. Its melting point was found to be 148–149°.

The analytical result of the substance is as follows:

0·1174 grm. substance gave 0·0264 grm. Pt on ignition.

	Calc. for $C_{34}H_{40}N_2Cl_6Pt$.	Found.
Platinum	22·08	22·49

Über die Legierungen des Tellurs mit Blei.

Von

Masao Kimura.

(Eingegangen am 5. März 1915.)

Nachdem Margottet[1] Bleitellurid von nicht wohl definierter Zusammensetzung durch das Zusammenschmelzen der beiden Komponenten erhalten hatte, haben Fay und Gillson[2] und Pélabon[3] über das System von Blei und Tellur genaue Untersuchungen angestellt. So ist festgestellt worden, dass es eine Verbindung PbTe, die nach Fay und Gillson bei 917°, und nach Pélabon bei 860° schmilzt, noch mit zwei Eutektika gibt. Trotz der Mühe dieser Verfasser bleibt die Frage, ob die Verbindung und die beiden Komponenten miteinander irgend eine Reihe von Mischkristallen bilden, gar nicht entschieden. Unter diesem gesichtspunkt habe ich darum die vorliegende Arbeit unternommen.

Das von mir gebrauchte Tellur schmilzt bei 441°, und das Blei bei 326°. Die beiden Materiale wurden für meinen Zweck der Untersuchung als rein genug wahrgenommen.

Die Gesamtmenge der beiden Elemente betrug bei allen Versuchen stets 20 g. Für die Legierungen mit 0—40% Pb bediente ich mich der Jenaer Glasröhrchen und für die weiteren der Meissener Porzellanröhrchen. Die Schmelzung geschah unter langsamem Einleiten von Wasserstoff. Um die Abkühlung der Schmelzen möglichst verlangsamen zu können, habe ich mir die Einrichtungen, die wir gewöhnlich in unserem Laboratorium brauchen, auch zu Nutz gemacht. Zur Temperaturbestimmung wurde das Pt—PtRh—Thermoelement von Heraeus verwandt, und um die vollkommene Homogenität der Mischung zu bewahren, wurde die Schmelze vor jeder Messung sorgfältig gerührt. Jede Abkühlungskurve wurde zweimal bestimmt, aus den gefundenen Temperaturen wurde das Mittel genommen.

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1 Thèse Paris, No. 422 (1879).

2 Amer. Chem. J., **27**, 81 (1902).

3 Ann. chim. phys., [8] **17**, 526 (1909).

Die Resultate der Versuche sind in der Tabelle I zusammengestellt, auf Grund deren das Zustandsdiagramm entworfen ist. Die Temperaturen sind im Massstabe von 10° = 1 mm, die Zeitdauer auf der eutektischen Horizontale im Massstabe von 40 Sek. = 1 mm. Das Zustandsdiagramm von Fay und Gillson wird auch zum Vergleich hier mit den Kreuzen und den sie verbindenden feineren Linien wiedergegeben.

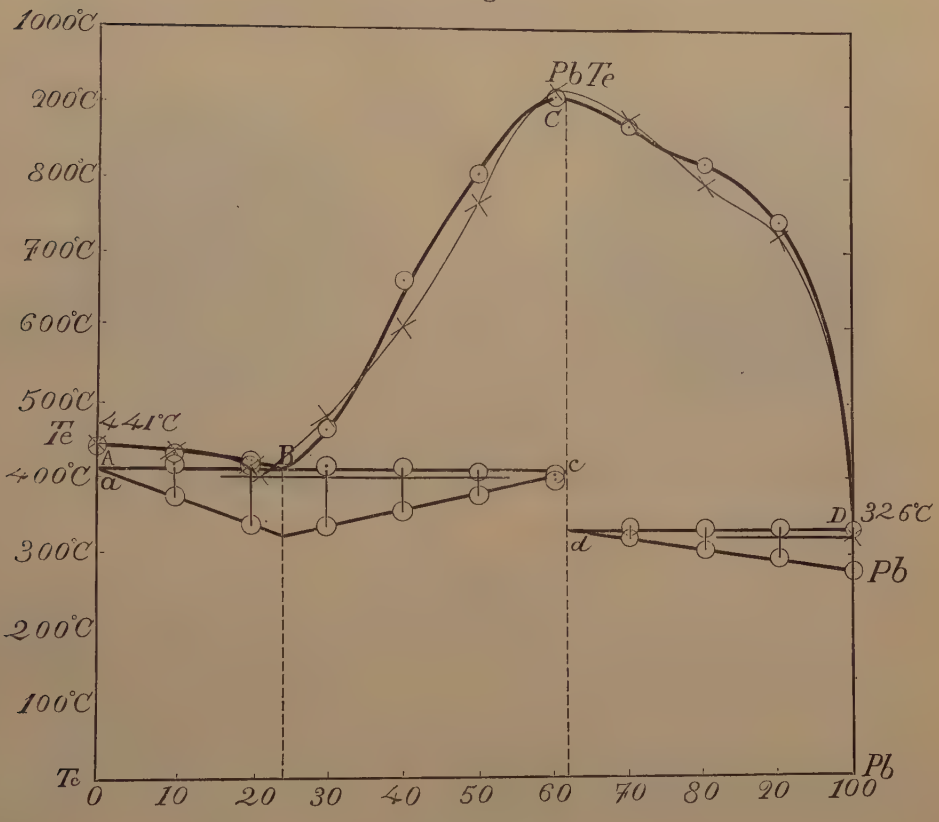
TABELLE I.

Bleigehalt im Gew.-%.	Temperaturen d. primären Kristallis. in °C.	Temperaturen d. eutekt. Kristallis. in °C.	Zeitdauer in Sekunden.
100.0	Schmelzpunkt des Bleis: 326°; Zeitdauer: 170″		
99.9	Nur mikroskopisch untersucht		
90.0	737	332	140
80.0	817	334	110
70.0	869	333	30
63.0	Nur mikroskopisch untersucht		
60.0	904	402	50
50.0	805	410	140
40.0	667	411	220
30.0	456	418	330
20.0	423	413	320
10.0	426	417	160
0.1	Nur mikroskopisch untersucht		
0.0	Schmelzpunkt des Tellurs: 441°; Zeitdauer: 216″		

Wie man sieht, ist mein Zustandsdiagramm nicht wesentlich anders als das von Fay und Gillson, nur mit einer sehr kleinen Differenz, was die beiden eutektischen Horizontalen betrifft.

Zwischen den Konzentrationen von 60—70% Pb, und zwar sehr nahe bei 60%, liegt ein Maximum auf der Kurve; für die Zusammensetzung der Verbindung Pb Te lässt sie sich als 61·89% Pb berechnen. Die Existenz dieser Verbindung wurde, wie schon erwähnt, von mehreren Verfassern bestätigt. Ich habe also nur mit den Reguli mit 60%, wie auch mit 63% Pb Näheres studiert. Beim ersten Regulus beginnt bei 904° die Erstarrung und es zeigt sich noch ein winziges Auftreten der eutektischen Kristallisation. Auf dem Schliffe sieht man mikroskopisch die wohl definierten Polygone der Verbindung, die von einer kleinen Menge des Eutektikums B umgeben sind; vergl. das

Zustandsdiagramm.



Lichtbild, Fig. 2. In gleicherweise sieht man auf dem Schliffe des Regulus mit 63% Pb die Polygone der Verbindung mit einer kleinen Menge des Bleis als Eutektikum auftreten; interessant ist hier, dass die Polygone, wenn geätzt, die wirkliche Struktur, welche aus blätterartigen Kristallen besteht, scheinbar macht; vergl. das Lichtbild, Fig. 3. Also muss die Zusammensetzung der Verbindung zwischen diesen beiden Konzentrationen liegen. Vermutlich liegt der Schmelzpunkt auch nicht sehr hoch über 904°. Aus der Tatsache, dass die Reguli mit 60% wie mit 62% Pb schon die Eutektika enthalten, folgt, dass bei der Verbindung mit Tellur oder mit Blei gar keine Mischkristalle zur Bildung kommen.

Das Eutektikum B besteht aus Tellur und der Verbindung, und zwar bei einer Konzentration von ca. 24% Pb und bei einer Temperatur

von 412°. Das Lichtbild, Fig. 1, entspricht der Struktur des Schliffs des Regulus mit 20% Pb, wo man schon das primär auskristallisierte, dunkel erscheinende Tellur deutlich erkennen kann. Bestätigt wurde auch mikroskopisch, dass sogar beim Regulus mit nur 0.1% Pb das Eutektikum auch noch auftritt. Infolgedessen muss sich die eutektische Horizontale nach links bis zur Konzentration des reinen Tellurs erstrecken, und daraus folgt, dass das Tellur sich mit der Verbindung in gar keiner Menge mischt.

Wie schon bekannt, tritt das Blei bei der Bleiseite der Konzentrationsachse als das Eutektikum auf. Auf dem Schliffe des Regulus mit nur 0·1% Te sieht man mikroskopisch die vom Blei umgebenen kleinen Tröpfchen der Verbindung. Daher kann man wohl sagen, dass das Blei sich mit der Verbindung gar nicht mischt. Das Lichtbild, Fig. 4, zeigt eine solche Struktur beim Regulus mit 90% Pb; die hell erscheinenden Teile entsprechen den schwer ätzbaren Kristallen der Verbindung.

Zusammenfassung.

1. In dem System existiert nur eine Verbindung Pb Te mit dem Schmelzpunkt von 904°.
2. Tellur und Blei bilden gar keine Reihen von Mischkristallen.
3. Es gibt ein Eutektikum, das bei 412° kristallisiert, und auch noch eins, das praktisch nicht anders als Blei ist.

Zum Schluss sei mir gestattet, Herrn Prof. Dr. M. Chikashige für seinen wertvollen Rat und Beistand meinen warmen Dank auszusprechen.

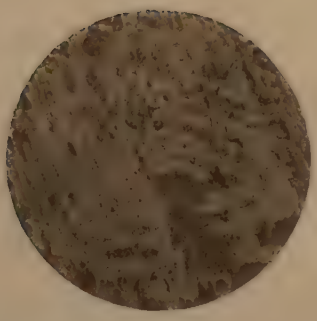


Fig. 1. Regulus mit 20% Pb; mit HNO_3 geätzt. 168 f. Vergr.

Fig. 2. Regulus mit 60% Pb; mit HNO_3 geätzt. 168 f. Vergr.

Fig. 3. Regulus mit 63% Pb; mit HNO_3 geätzt. 550 f. Vergr.

Fig. 4. Regulus mit 90% Pb; mit HNO_3 geätzt. 168 f. Vergr.

Metallographische Untersuchung über das System von Thallium und Selen.

Von

Takejiro Murakami.

(Eingegangen am 18. März 1915.)

Über die Legierungen von Thallium und Selen scheinen bisher nur die Angaben von Carstanjen[1] und Pélabon[2] veröffentlicht zu sein.

Nach Carstanjen bilden sich in diesem Systeme zwei Verbindungen. Die eine davon wird durch Zusammenschmelzen von 1 Äq. Thallium und 1 Äq. Selen ohne Feuererscheinung erhalten; sie ist schwarzfarbig, von schlackig blasiger Beschaffenheit, hart, spröde und ohne krystallinische Textur. Die andere wird durch Zusammenschmelzen von Thallium mit mehr als 1 und weniger als 3 Äq. Selen erhalten; die beiden Elemente vereinigen sich mit einander mit grosser Lebhaftigkeit und bilden gräulich schwarze, strahlig gruppierte, säulenförmige Krystalle. In dieser Beziehuug konnte der Verfasser nur bestätigen, dass die zwei Elemente sich mit einander legieren, aber gar nicht, dass sie wirklich einheitliche Verbindungen bilden würden.

Nach Pélabon, welcher das Zustandsdiagramm zuerst, aber noch sehr unvollkommen angestellt hat, verläuft die Liquidus von Thallium ausgehend zunächst horizontal, und zwar weit oberhalb des Schmelzpunktes des Thalliums, sodass man eine Trennung der zwei Schichten annehmen muss, und zwar bezeichnet Pélabon reines Thallium als die untere Schicht, und das Selenid Tl_2Se mit 16.22 Gew.-% Se als die obere. Bei weiterem Selenzusatz fällt die Liquidus, erreicht bei 23 Gew.-% Se einen eutektischen Punkt und steigt von hier an, bis bei 338° ein Maximum, das der Formel TlSe entspricht, erreicht wird. Pélabon gibt hierzu ohne Grund die weitläufigere Formel $Tl_2Se{\cdot}Tl_2Se_3$. Bei noch höheren Selengehalten fällt die Liquidus weiter steil ab, bis sie bei der Zusammensetzung von Tl_2Se_3 195° erreicht. Von hier an bleibt sie wieder konstant, sodass abermals die Ausbildung zweier

1 J. prakt. Chem., **102**, 79 (1867).

2 C. R., **145**, 118 (1907).

Schichten anzunehmen ist. Als die obere Schicht in diesem Gebiete bezeichnet er die Lösung eines Selenids in Selen, als die untere das oben genannte Selenid.

Im Folgenden habe ich auch wieder durch die thermische Analyse über das System zu untersuchen unternommen, ob ich das Pélabonsche Zustandsdiagramm noch etwas verbessern könne.

Das von mir gebrauchte Selen hatte den Schmelzpunkt von 217°, während das Thallium bei 287°, also etwas zu niedrig im Vergleich mit dem des sehr reinen Exemplars, schmolz.

Bei allen Versuchen nahm ich die beiden Elemente im genötigten prozentigen Verhältnisse, und zwar in den Mengen, die immer dasselbe Gesamtvolumen von 2·5 c.c. zeigten. Sie wurden in einem Schmelzrohr aus Jenaer Glas unter einem langsamen Wasserstoffstrome mit Hilfe eines Bunsenbrenners geschmolzen. Für die Temperaturbestimmung wurde das Silber-Konstantanthermoelement von Heraeus gebraucht und immer, bevor die wirkliche Messung geschah, wurde die Schmelze sorgfältig gerührt, um die vollkommene Homogenität der Mischung halten zu können. Die Abkühlung der Schmelze wurde in der gewöhnlich gebrauchten Weise möglichst verlangsamt. Jede Abkühlungskurve wurde zwei- oder dreimal bestimmt; aus den gefundenen Temperaturen und Zeitdauern wurde das Mittel genommen.

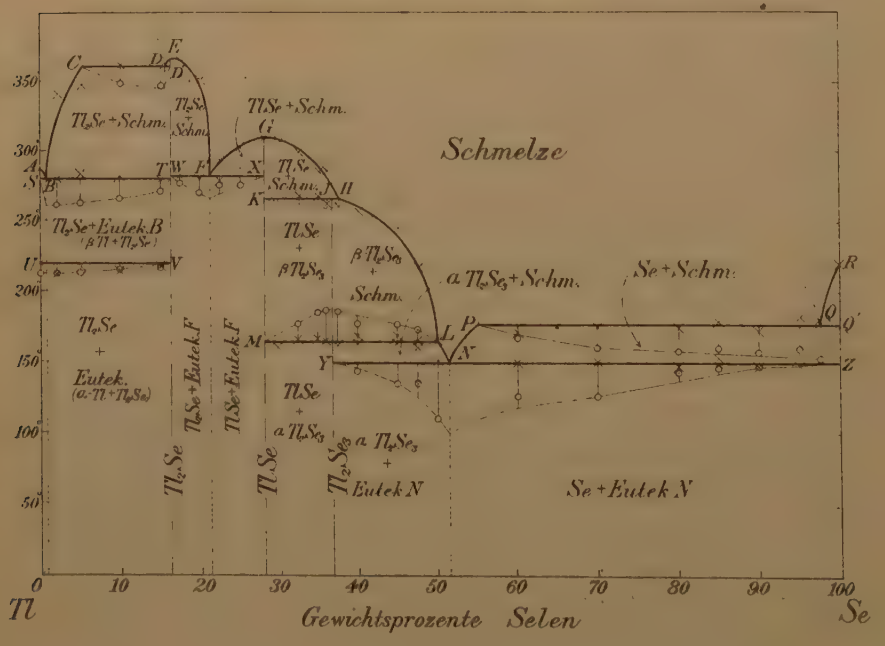


TABELLE I.

Se-Gehalt in Gew.-%	Primäre Kristallisation		Eutektische Kristallisation		Bildung von Tl_2Se_3		Umwandlung	
	Temp. in °C	Zeitdauer in Sek.	Temp. in °C	Zeitdauer in Sek.	Temp. in °C	Zeitdauer in Sek.	Temp. in °C	Zeitdauer in Sek.
0	284	120	—	—			219	30
2	341		280	130			212	30
5	347		284	120			217	30
10	362	90	282	100			214	20
15	361	100	279	60			217	15
17·5	365		283	40				
20	351		280	85				
22·5	294		278	45				
25	303		288	45				
28	310							
30	307						Spur	—
32·5	300				268	Spur	166	110
35	286				269	Spur	167	185
36	286				264	Spur	165	195
37·5	261						162	190
40	257		163	55			169	115
45	245		163	135			169	115
47·5	217		161	135			165	80
50	165		151	380				
60	172	130	150	215				
70	176	225	151	230				
80	175	250	148	60				
85	179	235	153	20				
90	173	265	148	15				
95	183	245	Spur	—				
97·5	180	325	Spur	—				
100	217	—	—	—				

Die Resultate der Versuche sind in Tabelle I zusammengestellt, auf Grund deren ist das Zustandsdiagramm entworfen.

Wie aus dem Diagramme ersichtlich, bildet Thallium mit Selen drei Verbindungen, deren Zusammensetzungen durch die Formeln Tl_2Se, TlSe und Tl_2Se_3 gegeben werden.

Die erste Formel Tl_2Se erfordert 16·26% Se; tatsächlich finden wir ein Maximum E in der Liquidus zwischen den beiden Kozentrationen 15–17·5% Se, und bei ca. 368°. Die Eigenschaften des Regulus mit der Zusammensetzung von 17·5% Se müssen denen der Verbindung sehr ähnlich sein. Er besteht aus einem spröden, nadelförmigen Kristalle und zeigt einem stahlähnlichen Glanz, welcher durch Anlaufen allmählich dunkler wird.

Die Verbindung Tl_2Se löst in der Schmelze Thallium höchstens zu ca. 1% (Lösung D), während das Thallium auch in der Sehmelze die Verbindung zu ca. 31% Tl_2Se (zu 5% Se entsprechend) löst (Lösung C). Diese Lösungen C und D mischen sich nicht mit einander und bilden in der Schmelze zwei Schichten. Durch Wärmeabnahme kristallisiert zunächst die Verbindung aus der mit C im Gleichgewicht stehenden Lösung D bei 361°. Die Lösung D wird in dieser Weise ganz aufgezehrt, bis endlich nur die Lösung C da bleibt. Die Reaktion geschieht bei einer konstanten Temperatur von 361°; dementsprechend bekommt man hier eine Horizontale CD. Wenn der Selengehalt weniger ist als 1%, so kristallisiert sich das Thallium aus dieser letzten Lösung primär aus; wenn er aber grösser ist als 1%, so scheidet sich diesmal das Tl_2Se primär aus. Bei 1% Se hat man das reine Eutektikum, welches aus Thallium und Tl_2Se besteht, und zwar bei 281° erstarrt. Die eutektische Horizontale erstreckt sich von S bis nach T; dementsprechend liegt noch wieder bei 217° die Umwandlungshorizontale des Thalliums.

Im Einklang mit diesen thermoanalytischen Resultaten findet man wirklich, dass alle Reguli von 5–15·5% Se immer aus zwei Schichten bestehen. Die obere Schicht besteht hauptsächlich aus der Verbindung Tl_2Se, welche sich mit der geringen Menge des Eutektikums B vermischt; vergl. Fig. 1, Taf. I. Die untere Schicht besteht hauptsächlich aus dem Eutektikum B, welches auch das Tl_2Se teilweise gemischt enthält.

Die zweite Verbindung TlSe erfordert den Gehalt an 27·97% Se. Der Regulus mit 28% Se wurde hergestellt; er hat den Schmelzpunkt von 310°, welcher in dieser Gegend der Kurve dem Maximum ent-

spricht. Das Schliff des Regulus zeigt unter dem Mikroskop eine ganz homogene Struktur; vergl. Fig. 2, Taf. I. Der Regulus ist auch spröde, aber etwas zäher als die erste Verbindung, dunkelgrau, von nadelförmigen Kristallen, und verliert seinen Glanz in der trocknen Luft nicht.

Die Verbindung TlSe mischt sich lediglich mit der ersten Tl_2Se in der Schmelze. Wenn der Selengehalt geringer ist als 21%, so scheidet aus der Schmelze durch Wärmeentziehung die Verbindung Tl_2Se primär aus; wenn er aber grösser ist als 21%, dann scheidet sich die Verbindung TlSe primär aus. Die Temperatur der primären Ausscheidung von Tl_2Se wird mit der wachsenden Menge des Selens schnell erniedrigt, bis die schliesslich beim Punkt F mit der Konzentration von 21% Se 283° erreicht. Von diesem Punkt an steigt wieder die Temperatur, bis sie bei G das Maximum erreicht. Das Eutektikum besteht also aus 40·5% TlSe und 59·5% Tl_2Se. Die eutektische Horizontale erstreckt sich von W bis X; so schliesst man, dass kein Mischkristall in jeder Seite der beiden Verbindungen entsteht. Diese Resultate werden alle durch die mikroskopischen Untersuchungen gut bestätigt: vergl. Fig. 3 und Fig 4, Taf. I.

In dem Falle, wo die Verbindung TlSe in der Schmelze mit dem geschmolzenen Selen zusammengemischt bleibt, scheidet sie sich aus dieser Lösung durch Wärmeentziehung primär aus. Die Temperatur der Ausscheidung wird mit der wachsenden Menge des Selens allmählich erniedrigt, bis sie schliesslich beim Punkt H mit der Konzentration von 37·5% Se ca. 265° erreicht. Bei dieser Temperatur reagiert die Verbindung TlSe mit dem Selen, um die Verbindung β-Tl_2Se_3 nach der folgenden Gleichung zu bilden:

$$2\,TlSe + Se = Tl_2Se_3.$$

Hier liegt eine Horizontale HK, welche diesen chemischen Vorgang wohl repräsentiert. Aus der Formel Tl_2Se_3 berechnet man die Zusammensetzung als 36·80% Se. Nenne man den dieser Konzentration und Temperatur entsprechenden Punkt J, wo der Regulus gänzlich nur aus der reinen Verbindung bestehen wird. Von J nach links wird die Zeitdauer der Reaktion allmählich kleiner, bis sie endlich bei K Null wird. Die sämtlichen Reguli in dieser Gegend müssen also aus dem Gemisch von TlSe und Tl_2Se_3 bestehen, wie es wohl durch die mikroskopischen Untersuchungen bestätigt wird; vergl. Fig. 5, Taf. II.

Von J nach rechts wird TlSe nicht mehr existieren, weil es sich

mit Selen gänzlich ins β-Tl_2Se_3 umwandeln wird; es bleibt aber noch der Überschuss von Selen ausser Reaktion. Sonach muss sich die Umwandlungshorizontale von J bis nach H erstrecken. Unterhalb der Temperatur von 265° kann die Verbindung β-Tl_2Se_3 in der Schmelze ohne Zersetzung bleiben; sie löst sich im Überschuss von Selen auf, und daraus scheidet sie sich bei der Abkühlung primär aus.

Die β-Verbinduug umwandelt sich bei 165° in die α-Form um, und daher entsteht hier wieder eine Horizontale ML; auf der Linie hat man die Stelle der maximalen Zeitdauer gerade bei der Zusammensetzung der Verbindung gefunden.

Die Verbindung α-Tl_2Se_3 kristallisiert in stahlgrauen Nadeln, fast ähnlich wie TlSe, aber nur etwas zäher.

α-Tl_2Se_3 mischt sich auch gut mit Selen in der Schmelze; es scheidet sich bei der Abkühlung primär aus, indem die Temperatur allmählich bis zu 150° zum Abfallen kommt. Bei der letzten Temperatur, wo die Konzentration des Selens ca. 52% ist, scheidet sich die Verbindung nicht mehr primär aus; statt dessen kristallisiert hier das reine Eutektikum N, das aus 76% Tl_2Se_3 und 24% Se besteht, aus.

Bei den Konzentrationen zwischen 52–55% Se mischt sich α-Tl_2Se_3 mit Se in der Schmelze. Wenn aber die Konzentration des Selens grösser wird als 55%, dann wird die Verbindung nicht mehr mit dem Selen vollkommen mischbar sein. In der Tat löst die Verbindung Selen in der Schmelze zu ca. 28·8% (Lösung P), während das Selen die Verbindung auch in der Schmelze zu ca. 4% löst (Lösung Q). Diese Lösungen P und Q mischen sich nicht mit einander, und daher bilden sie in der Schmelze zwei Schichten. Durch Wärmeentziehung kristallisiert zunächst das Selen aus der Lösung Q konstant bei 177°. Nachdem die Lösung Q in dieser Weise gänzlich aufgezehrt ist, beginnt die Lösung P durch Wärmeentziehung wieder das Selen ausscheiden zu lassen, im weiteren Laufe fällt die Temperatur schliesslich zu 150° ab. Bei dieser Temperatur kommt der Rest der Schmelze gerade im Verhältnis der eutektischen Zusammensetzung zu stehen. Bei weiterer Wärmeentziehung erstarrt das Eutektikum bei derselben Temperatur; uud die eutektische Horizontale erstreckt sich einerseits bis nach der Konzentration der Verbindung Tl_2Se_3 und anderseits bis nach dem reinen Selen.

Durch die mikroskopischen Untersuchungen wurden die obigen Resultate auch vollkommen bestätigt. Die Reguli mit 36·8–52% Se bestehen aus der Verbindung Tl_2Se_3, die durch das Eutektikum umgeben

ist; vergl. Fig. 6, Taf. II. Die Reguli mit 55–97·5% Se bilden immer zwei Schichten; die obere Schicht besteht hauptsächlich aus dem Selen, wie Fig. 7. Taf. II zeigt; die untere Schicht besteht hauptsächlich aus dem Eutektikum, während das Selen sich inzwischen im kristallisierten Zustande vermischt, wie auch Fig. 8 und Fig. 9, Taf. II zeigt.

Zusammenfassung:

1. Thallium und Selen bilden miteinander drei Verbindungen Tl_2Se, TlSe und Tl_2Se_3.

2. Tl_2Se besteht aus spröden, dunkelgrauen nadelförmigen Kristallen mit dem Schmelzpunkt von ca. 368°.

3. Tl_2Se löst in der Schmelze Thallium höchstens zu 1%, während das Thallium die Verbindung Tl_2Se auch höchstens zu 31% löst. Man hat also zwischen den Konzentrationen 9·5–85·5% Tl zwei Flüssigkeitsschichten, aus welchen, nachdem die Verbindung sich primär ausgeschieden hatte, dann sich das Eutektikum bei 281° ausscheiden lässt.

4. TlSe schmilzt bei 310°. Sie ist ganz ähnlich wie Tl_2Se, aber nur etwas zäher.

5. TlSe mischt sich mit Tl_2Se lediglich in der Schmelze, gar nicht aber im festen Zustande. So bilden die beiden mit einander bei 283° ein Eutektikum.

6. TlSe reagiert mit dem geschmolzenen Selen bei 265° und bildet die Verbindung β-Tl_2Se_3, die sich bei 165° in α-Form umwandelt. Die letzte Verbindung sieht sehr ähnlich aus wie die erste.

7. Tl_2Se_3 löst Selen in der Schmelze zu 28·8%, während das Selen Tl_2Se_3 zu 4% löst. Daher entstehen bei den Reguli von 55–97·5% Se immer zwei Schichten. Aus der homogenen Lösung scheidet sich Selen oder Tl_2Se_3 primär aus, und der Rest der Schmelze kristallisiert sich als Eutektikum bei 150°.

Es sei mir gestattet, an dieser Stelle Herrn Prof. Dr. M. Chikashige meinen Dank auszusprechen, sowohl für die Anregung zu dieser Arbeit, wie auch für seine Freundlichkeit, mich während der Ausführung desselben mit mannigfachen wertvollen Ratschlägen unterstützt zu haben.

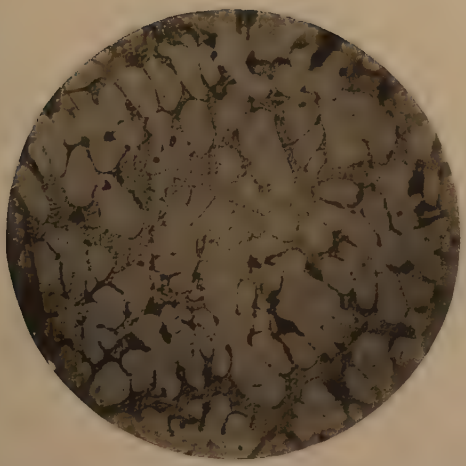


Fig. 1. Die obere Schicht beim Regulus mit 10% Se; wo TlSe sich mit dem Eutektikum B vermischt; geätzt mit verd. HNO_3.
250 f. Vergr.

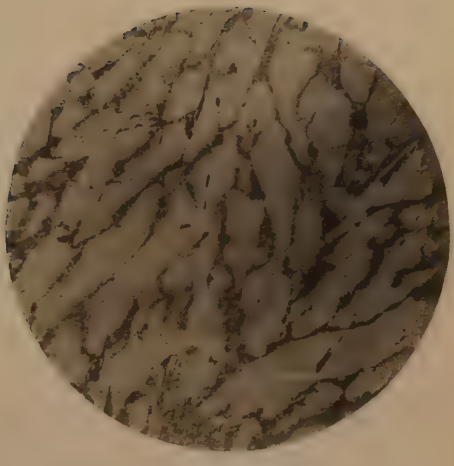


Fig. 2. Regulus mit 28% Se; TlSe.
250 f. Vergr.

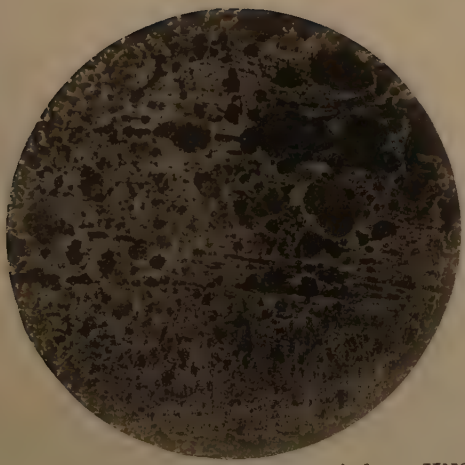


Fig. 3. Regulus mit 20% Se; geätzt mit konz. HNO_3; Tl_2Se + Eutektikum.
250 f. Vergr.

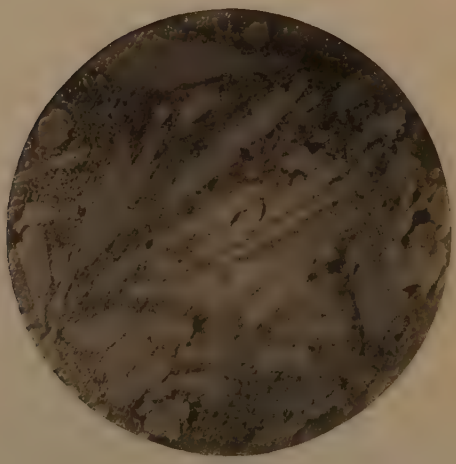


Fig. 4. Regulus mit 25% Se; geätzt mit konz. HNO_3; TlSe + Eutektikum.
250 f. Vergr.

Fig. 5 Regulus mit 35% Se; geätzt mit konz. HNO_3: $TlSe + Tl_2Se_3$.
250 f. Vergr.

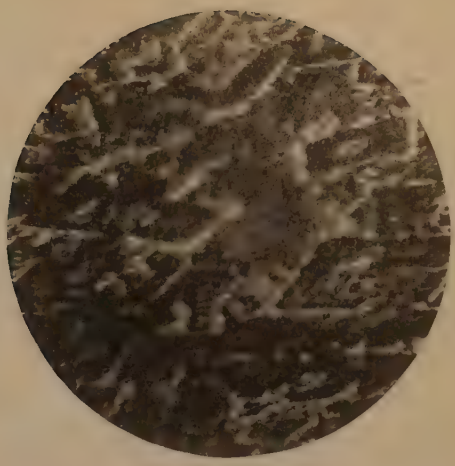


Fig. 6. Regulus mit 47·5% Se; geätzt mit konz. HNO_3: Tl_2Se_3 + Eutektikum.
250 f. Vergr.

Fig. 7. Selenschicht beim Regulus mit 90% Se;
250 f. Vergr.

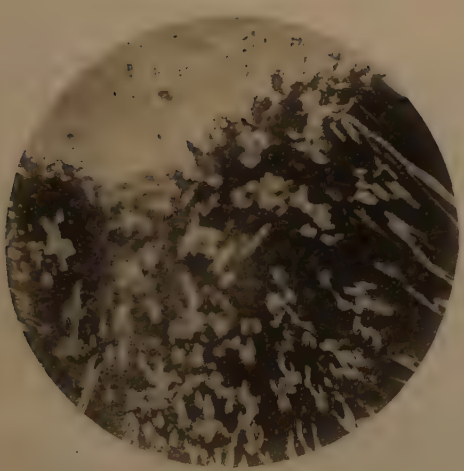


Fig. 8. Eutektikumschicht beim Regulus mit 80% Se; an der Grenze; geätzt mit konz. HNO_3.
250 f. Vergr.

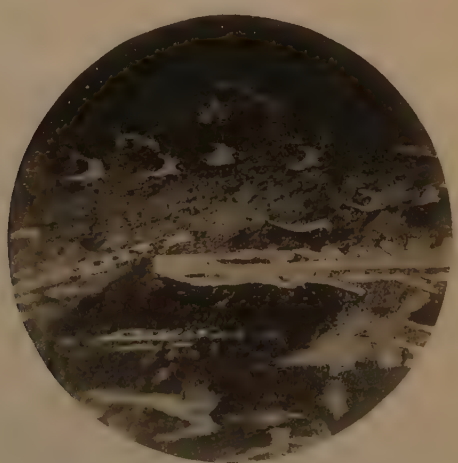


Fig. 9. Eutektikumschicht beim Regulus mit 90% Se; geätzt mit konz. HNO_3.
250 f. Vergr.

On Extreme Ways and Curves of Extreme Value of Holomorphic Functions.

By

Toshizô Matsumoto.

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Let $Z=f(z)$ be a holomorphic function of z in a certain region of Gauss' plane, then we can expand the function about any point e.g. z_0 in the region into a power-series of $z-z_0$:

$$Z-Z_0=a_1(z-z_0)+a_2(z-z_0)^2+\dots,$$

where Z is the value of the function at $z=z_0$. If we write Z for $Z-Z_0$ and z for $z-z_0$, the series becomes

$$Z=a_1z+a_2z^2+\dots.$$

When a_1 is not zero, by the elementary theorem of the Theory of Functions, z can also be expanded as a power-series of Z,

$$z=A_1Z+A_2Z^2+\dots, \qquad A_1\neq 0.$$

Such a function as Z of z, we shall hereafter call a *reversibly holomorphic* function about the origin $z=0$.

Since for such a function, $\frac{dZ}{dz}$ does not vanish about the origin a circle about it is easily proved to be transformed by means of $Z=f(z)$ into a closed regular curve about the origin $Z=0$ of the plane of Z. Therefore when the absolute value $|Z|$ of Z is not equal to a constant, $|Z|$ must take at least a maximum and a minimum value on the circle. The locus of the point z_0 at which $|Z|$ is extreme, when z runs concentric circles, is the object of the present study. In the following we assume $Z=f(z)$, $(f(0)=0)$, to be reversibly holomorphic about the origin; and only this small region is taken into consideration.

1. The locus of the point z_0 at which $|Z|$ takes an extreme value when z describes a circle with the variable radius, whose centre is at

the origin, is defined as an *extreme way* of the function, while the corresponding locus of $Z(z_0)$ in the plane of Z is defined as a *curve of extreme value*. For maximum values, *maximum ways* resp. *curves of maximum value* are used and for minimum values, similar definitions. In the following, the relations between the ways and curves are discussed.

2. As usual in a reversibly holomorphic function, put

$$\begin{aligned} &Z = a_1 z + a_2 z^2 + \dots , && a_1 \neq 0, \\ &z = x + iy, \ x = r\cos\theta, && y = r\sin\theta, \\ &Z = X + iY, \ X = R\cos\theta, && Y = R\sin\theta. \end{aligned}$$

It is known and easily proved that X as well as Y can be expanded into a Taylor's series of x and y about $(0|0)$, and hence of r and θ.

Putting $$R^2(x,y) = \varphi(r,\theta),$$

$$\varphi(r,\theta+h)=\varphi(r,\theta)+\varphi_\theta'(r,\theta)\frac{h}{1!}+\dots+\varphi_\theta^{(2n-1)}(r,\theta)\frac{h^{2n-1}}{(2n-1)!}$$

$$+\varphi_\theta^{(2n)}(r,\theta)\frac{h^{2n}}{(2n)!}+\dots .$$

When θ changes from o to 2π, with respect to the circle $x^2+y^2=r_0^2$, R, therefore $\varphi(r_0,\theta)$ returns to its original value, hence it must take at least a maximum (resp. a minimum) value for certain θ, say θ_0 and assume that

$$\varphi_\theta'(r_0,\theta_0)=\dots=\varphi_\theta^{(2n-2)}(r_0,\theta_0)=0,$$

and $$\varphi_\theta^{(2n-1)}(r_0,\theta_0)=0, \ \varphi_0^{(2n)}(r_0,\theta_0)\neq 0,$$

where n is an integer greater than or equal to 1. Suppose that these relations hold for parametric values of r about r_0, e.g., in an interval I_1 and for corresponding values of θ_0: then consider the function $\varphi^{(2n-1)}(r,\theta)$. This function satisfies the relations

$$\varphi_\theta^{(2n-1)}(r_0,\theta_0)=0, \ \varphi_\theta^{(2n)}(r_0,\theta_0)\neq 0,$$

hence we obtain a continuous function $\theta=\psi(r)$ in a certain interval about r_0, say I_2. Let I be the smaller of the two intervals I_1 and I_2, then we have for r in I,

$$\varphi_\theta'(r,\psi(r))=\dots=\varphi_\theta^{(2n-1)}(r,\psi(r))=0,$$

$$\varphi_\theta^{(2n)}(r, \psi(r)) \neq 0, \quad \theta_0 = \psi(r_0).$$

Now put

$$\varphi^{(2n-1)}(r, \theta) \equiv F(r, \theta),$$

then $\psi(r)$ is the continuous solution for $r=r_0, \theta=\theta_0$ of the differential equation

$$\frac{\partial F}{\partial r} + \frac{\partial F}{\partial \theta}\frac{d\theta}{dr} = 0,$$

where $\frac{\partial F}{\partial r}, \frac{\partial F}{\partial \theta}$ are power-series of r and θ. Moreover $\frac{\partial F}{\partial \theta}$ does not vanish in I. Hence $\theta=\psi(r)$ will be obtained as a power-series of r in I. The equation of the extreme way is, therefore,

$$\xi = r\cos\{\psi(r)\}, \quad \eta = r\sin\{\psi(r)\}, \text{ about } r_0;$$

and

$$d\xi^2 + d\eta^2 = (1 + r^2\psi'^2)\, dr^2.$$

So the extreme way is a regular curve. From the properties of the reversibly holomorphic function, the corresponding curve of extreme value is also a regnlar curve whose equation is

$$\Xi = R(r, \psi(r))\cos\{\Theta(r, \psi(r))\},$$
$$H = R(r, \psi(r))\sin\{\Theta(r, \psi(r))\}.$$

Thus, if our conditions are satisfied. we see that in this case the following relations must be established:

$$\varphi_\theta'(r, \theta) = \{\theta - \psi(r)\}^{2n-1} K_1(r, \theta),$$
$$\ldots = \ldots$$
$$\varphi_\theta^{(2n-1)}(r, \theta) = \{\theta - \psi(r)\}\, K_{2n-1}(r, \theta),$$

where the functions K do not vanish in the neighborhood of (r_0, θ_0). But if for only the point (r_0, θ_0),

$$\varphi_\theta'(r_0, \theta_0) = \ldots = \varphi_\theta^{(2n-1)}(r_0, \theta_0) = 0,$$

while

$$\varphi_\theta^{(2n)}(r_0, \theta_0) \neq 0.$$

Then from the differential equation

$$\varphi_\theta'' + \frac{dr}{d\theta}\frac{\partial \varphi_\theta'(r, \theta)}{\partial r} = 0,$$

we obtain the solution:

$$r-r_0 = A_{2n-1}(\theta-\theta_0)^{2n-1} + A_{2n}(\theta-\theta_0)^{2n} + \dots ,$$

provided $$\frac{\partial \varphi_0'(r_0, \theta_0)}{\partial r} \neq 0 ;$$

whence it follows that

$$\theta-\theta_0 = B_1(r-r_0)^{\frac{1}{2n-1}} + B_2(r-r_0)^{\frac{2}{2n-1}} + \dots .$$

This solution represents $2n-1$ determinations. If all the coefficients of a certain determination $P(r-r_0)$ for $r>r_0$ be real, then by the analytical continuation about r_0, we can find another determination $Q(r_0-r)$ for $r_0>r$, whose coefficients are all real. Hence before and after r_0, we shall obtain a real extreme way. Therefore when the number of the extreme ways changes, we must have at least

$$\frac{\partial \varphi_0'(r, \theta)}{\partial r} = 0.$$

From such an equation we will obtain in general solutions of the type,

$$\theta-\theta_0 = \theta(t),^1$$
$$r-r_0 = r(t).$$

Among these will be given several extreme ways. As illustration consider the following function :

$$Z = z - z^3.$$

The analytic continuation of the function to the point $z=\frac{1}{3}$ gives :

$$Z = \frac{8}{27} + \frac{2}{3}(z-\tfrac{1}{3}) - (z-\tfrac{1}{3})^2 - (z-\tfrac{1}{3})^3.$$

Writing the series as usual :

$$Z = \frac{2}{3}z - z^2 - z^3,$$

reversibly holomorphic about $z=0$, $Z=0$.

Now $$R^2 = \frac{4}{9}r^2 - \frac{4}{3}r^3\cos\theta - \frac{4}{3}r^4\cos 2\theta + 2r^5\cos\theta + r^4 + r^6,$$

1 See e.g., E. Picard : Traite D'analyse III, pp. 36.... .

putting $u \equiv \frac{3}{2r^3} R^2$,

$$\frac{\partial u}{\partial \theta} = \sin\theta\,(2 + 8r\cos\theta - 3r^2) = 0.$$

The roots are $\theta = 0,\ \pi$

and $$\cos\theta = \frac{3r^2 - 2}{8r}.$$

i) when r is sufficiently small, the roots are o and π:

and $$\left(\frac{\partial^2 u}{\partial \theta^2}\right)_{\theta=0} = 2 + 8r - 3r^2 > 0 \ldots \text{min.},$$

$$\left(\frac{\partial^2 u}{\partial \theta^2}\right)_{\theta=\pi} = -2 + 8r + 3r^2 < 0 \ldots \text{max.},$$

i.e., we have only a maximum way $\theta = \pi$ and a minimum way $\theta = 0$.
ii) when r is not so small, adding to the above extreme ways, we have

$$\cos\theta = \frac{3r^2 - 2}{8r}.$$

From the condition

$$|\cos\theta| \leqq 1,$$

we have $$3r^2 + 8r - 2 \geqq 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1),$$

$$-3r^2 + 8r + 2 \geqq 0 \ldots\ldots\ldots\ldots\ldots\ldots \quad (2);$$

from (1), $$r \geqq \frac{\sqrt{22} - 4}{3} \equiv r_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3),$$

$$\cos\theta_{r_1} = -1,\ \theta_{r_1} = \pi,$$

and from (2), $$r \leqq \frac{\sqrt{22} + 4}{3} \equiv r_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4).$$

$$\cos\theta_{r_2} = +1,\ \theta_{r_2} = 0.$$

By easy calculations,

$$\left(\frac{\partial^2 u}{\partial \theta^2}\right)_{\substack{\theta=\pi \\ r=r_1}} = \left(\frac{\partial^2 u}{\partial \theta^2}\right)_{\substack{\theta=0 \\ r=r_2}} = \left(\frac{\partial^3 u}{\partial \theta^3}\right)_{\theta=0,\,\pi} = 0,$$

$$\left(\frac{\partial^4 u}{\partial \theta^4}\right)_{r=r_1,\,r=r_2} \neq 0.$$

These results show, (Fig. 1), that the x-axis is a minimum way from O to Q, $(OQ=r_2)$; a maximum way from O to $P(OP=r_1)$; the circle $APBQ$ whose equation is $3r^2-8r\cos\theta-2=0$ represents two maximum ways; PR, a minimum way. At P and Q the number of the extreme ways changes, so we have,

$$\left(\frac{\partial^2 u}{\partial r\,\partial\theta}\right)_{\substack{r=r_1,\ r=r_2\\ \theta=\pi,\ \theta=0}} = 0,$$

moreover we notice that P is a maximum point.

z-plane.

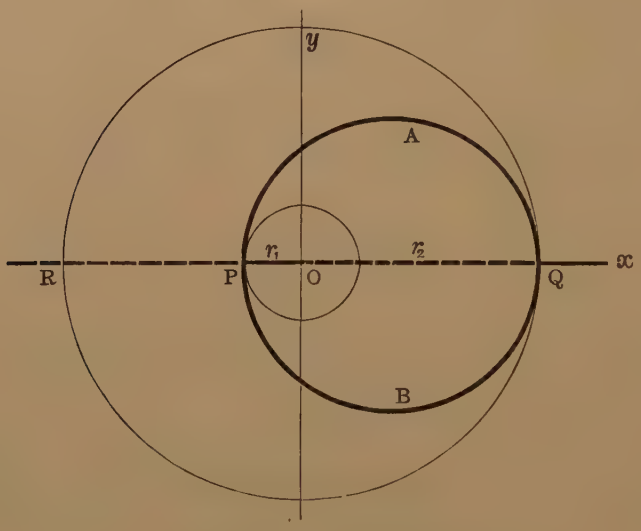

Fig. 1.

3. Let Γ be the curve in Z-plane corresponding to a circle γ in z-plane, ω being the angle between the radius vector and the tangent to Γ, we have

$$\tan\omega = \frac{Rd_0\theta}{d_0R}.$$

When R is extreme, d_0R vanishes; but $d_0\theta$ does not vanish; for if it vanish, from

$$\theta = \arctan\left(\frac{Y}{X}\right),$$

we must have

$$X\frac{\partial Y}{\partial \theta} - Y\frac{\partial X}{\partial \theta} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1),$$

from $d_\theta R = 0$,

$$X\frac{\partial X}{\partial \theta} + Y\frac{\partial Y}{\partial \theta} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2).$$

By (1) and (2)

$$\left(\frac{\partial X}{\partial \theta}\right)^2 + \left(\frac{\partial Y}{\partial \theta}\right)^2 = 0.$$

Hence

$$\frac{\partial X}{\partial \theta} = -r\sin\theta\frac{\partial X}{\partial x} + r\cos\theta\frac{\partial X}{\partial y} = 0$$

$$\frac{\partial Y}{\partial \theta} = -r\sin\theta\frac{\partial Y}{\partial x} + r\cos\theta\frac{\partial Y}{\partial y} = 0,$$

which leads to the equation:

$$\left(\frac{\partial X}{\partial x}\right)^2 + \left(\frac{\partial Y}{\partial x}\right)^2 = \left|\frac{dZ}{dz}\right|^2 = 0,$$

which is impossible. We have $\omega = \frac{\pi}{2}$; i.e., the radius vector R is perpendicular to the curve Γ at the point of an extreme value.

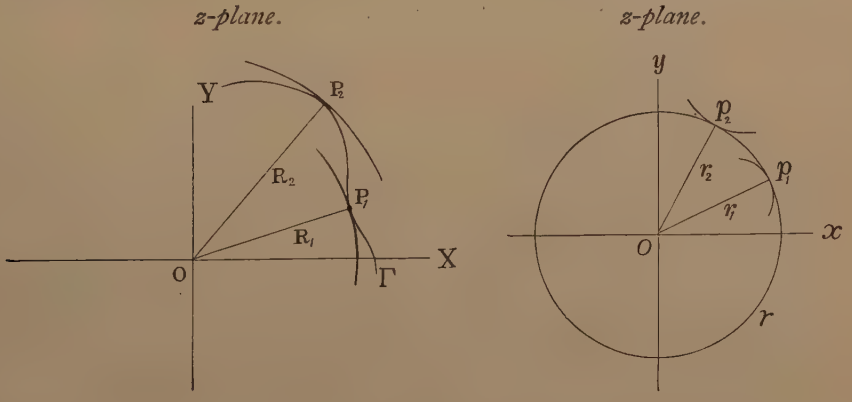

Fig. 2.

Fig. 2 shows that for $z = p_1$, $Z = P_1$, R is minimum; for $z = p_2$, $Z = P_2$, R is maximum. Since R is perpendicular to Γ at P, the part of the circle with centre O, which is drawn to touch the curve Γ at P, lies on one side of Γ, so also is its corresponking curve in z-plane. When P_1 is the point of minimum value, then the part of the circle

lies within Γ, touching it; therefore the corresponding curve in z-plane lies within γ and touches it at p_1; i.e., op_1 is maximum in the neighborhood of p_1; the same is true for every point of the locus of P_1. For P_2, op_2 is minimum; hence

a). *The curve of minimum (maximum) value of the functiou* $Z=Z(z)$ *is the maximum (minimum) way of the function* $z=z(Z)$.

b). *The minimum (maximum) way of the function* $Z=Z(z)$ *is the curve of maximum (minimum) value of the function* $z=z(Z)$.

4. Example. $Z=z(2-z)$.

This function is reversibly holomorphic in the circle with radius $=1$ about the origin.

$$R^2 = r^2(4-4r\cos\theta+r^2),$$

$$\frac{\partial R^2}{\partial\theta} = 4r^3\sin\theta = 0,\ \theta = 0 \text{ or } \pi.$$

For

$$\theta = 0, \quad R_0 = r(2-r) \ldots \text{min.}$$

$$\theta = \pi_1 \quad R_\pi = r(2+r) \ldots \text{max.}$$

In Fig. 3 (right), the dotted line is the minimum way; the thick line the other. In Fig 3 (left),, the curve of minimum value is given by the dotted line, the other by the thick line.

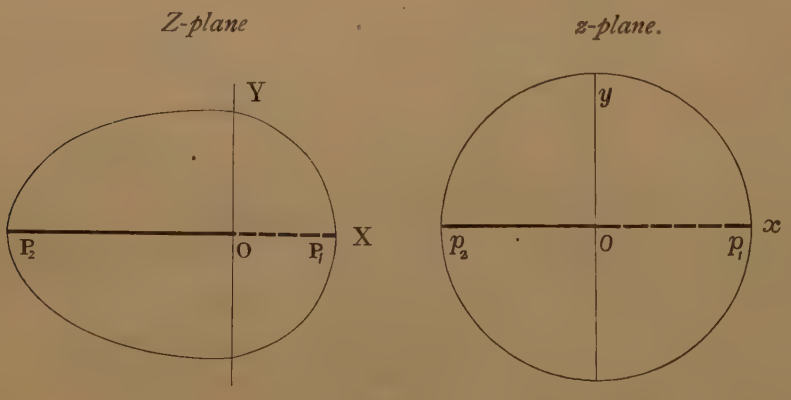

Fig. 4.

The reciprocal function is

$$z = 1-\sqrt{1-Z}\,.$$

When R is sufficiently small (Fig. 4).

For $\theta = 0,\ r_0 = 1-\sqrt{1-R}$ ... max.,

$\theta = \pi,\ r_\pi = \sqrt{1+R}-1$ ... min.

op_1 is the curve of maximum value; OP_1, the maximum way.

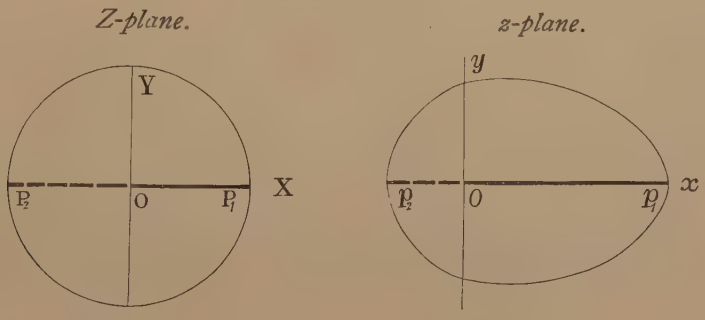

Fig. 4.

5. Next we shall find the number of the extreme ways and of the curves of extreme value of the function about the origin:

$$Z = a_1 z + a_2 z^2 + \ldots, \quad a \neq 0.$$

Put $a_1 = \rho_1 e^{i\alpha_1}, \ldots a_n = \rho_n e^{i\alpha_n}, \ldots .$

Then $$X = \sum_{n=1}^{\infty} \rho_h r^h \cos(h\theta + \alpha_h),$$

$$Y = \sum_{k=1}^{\infty} \rho_k r^k \sin(k\theta + \alpha_k)$$

Hence $$XX_\theta' + YY_\theta' = \left\{\sum_{h=1}^{\infty} \rho_h r^h \cos(h\theta+\alpha_h)\right\}\left\{-\sum_{k=1}^{\infty} k\,\rho_k r^k \sin(k\theta+\alpha_k)\right\}$$

$$+ \left\{\sum_{k=1}^{\infty} \rho_k r^k \sin(k\theta+\alpha_k)\right\}\left\{\sum_{h=1}^{\infty} h\,\rho_h r^h \cos(h\theta+\alpha_h)\right\}$$

$$= \sum_{h,\,k=1}^{\infty} (h-k)\,\rho_h \rho\ r^{h+k} \cos(h\theta+\alpha_h)\sin(k\theta+\alpha_k)$$

Changing h into k, k into h, and adding we obtain

$$2\,(XX_0' + YY_0') = \sum_{h,\,k=1}^{\infty} (h-k)\,\rho_h\,\rho_k\,r^{h+k} \sin\left\{(k-h)\,\theta + a_k - a_h\right\}.$$

We may divide the double sum into three parts of

i) sum of terms for $h=k$, (equal to zero),

ii) sum of terms for $h < k$,

iii) sum of terms for $h > k$.

If we interchange h and k, the third sum is equal to the second. Therefore we obtain

$$XX_0' + YY_0' = \sum_{h,\,k=1}^{\infty} (h-k)\,\rho_h\,\rho_k\,r^{h+k} \sin\left\{(k-h)\,\theta + a_k - a_h\right\},$$

where h and k take all positive integers $k > h$.

Let a_n be the first coefficient (except a_1) which does not vanish, then

$$XX_0' + YY_0' = (1-n)\,\rho_1\,\rho_n\,r^{n+1} \sin\{(n-1)\,\theta + a_n - a_1\} + \ldots;$$

for the extreme value, this must vanish even for very small r, therefore in the limit,

$$\sin\{(n-1)\,\theta + a_n - a_1\} = 0.$$

The roots of the equation are given by

$$\frac{m\pi + a_1 - a_n}{n-1},\quad m = 0, 1, 2, \ldots 2n-3.$$

All the roots give extreme values for small r, since for these values

$$\frac{\partial}{\partial\theta}(XX' + YY_0') \neq 0.$$

Hence, *the number of the extreme ways and that of the curves of extreme value are each equal to* $2(n-1)$, *where the nth coefficient is the first one not zero. Moreover by the conformity of the function, the angle between two consecutive ways is equal to that of the corresponding curves of extreme value.*

In Fig. 5, the dotted lines represent the minimum ways resp. the curves of minimum value of the function,

$$Z = z\,(1 - z^4);$$

the thick lines, those of maximum.

$$R\,\text{min.} = r\,(1 - r^4),$$
$$R\,\text{max.} = r\,(1 + r^4).$$

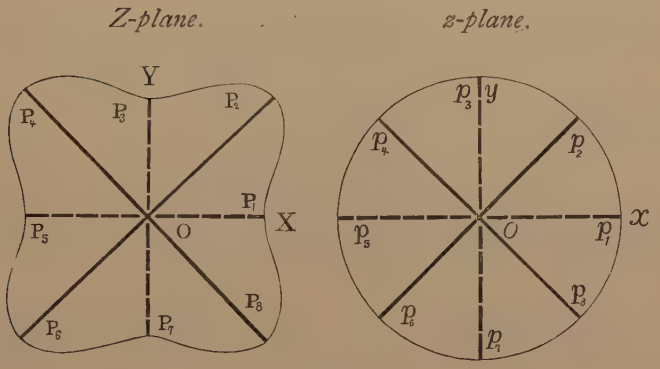

Fig. 5.

Fig. 6 is for the inverse function of the above, approximately. The number of the ways is 8.

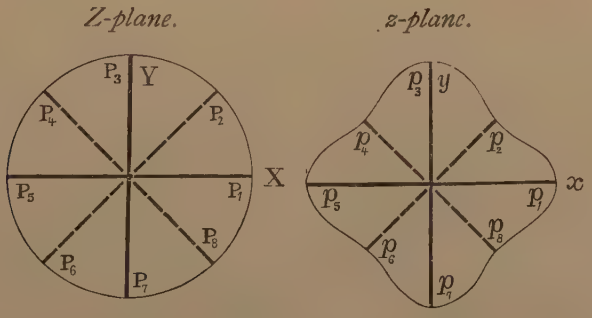

Fig. 6.

6. Let us call a power-series with real coefficients, which is reversible, a *real power-series;* then a *real power-series has the x-axis for an extreme way and the X-axis, for the corresponding curve of extreme value and vice versa.* For sueh a function is symmetrical with respect to the x- resp. X-axis.

When a reversibly holomorphic function $Z = a_1 z + a_2 z^2 + \ldots$ *has the x-axis for extreme way, then the quotients:*

$$\frac{a_2}{a_1}, \frac{a_3}{a_1} \cdots$$

are all real and vice versa.

For suppose a_n the first coefficient (except a_1) not zero, in the formula of §5 put $\theta=0$ (or π),

$$XX_\theta' + YY_\theta' = (1-n)\, r^{n+1}\rho_1\rho_n \sin(a_n - a_1) - nr^{n+2}\rho_1\rho_{n+1}\sin(a_{n+1}-a_1)+\cdots$$

$$= 0.$$

Diminishing r we must have,

$$a_n - a_1 = m_{n,1}\,\pi,$$

where $m_{n,1}$ is an integer; hence

$$a_{n+i} - a_1 = m_{n+i,1}\,\pi, \qquad i = 0, 1, 2, \ldots n-1, \quad \ldots\ldots \quad (1)$$

moreover the coefficient of r^{2n+s},

$$(1-\overline{2n+s-1})\rho_1\rho_{2n+s-1}\sin(a_{2n+s-1}-a_1)+(n-\overline{n+s})\rho_n\rho_{n+s}\sin(a_n-a_{n+s})+\cdots$$

is equal to zero; then by (1), we have

$$a_{n+i} - a_1 = m_{n+i,1}\,\pi,$$
$$a_{n+j} - a_1 = m_{n+j,1}\,\pi.$$

Therefore $a_{n+j}-a_{n+i}$ is a multiple of π, hence

$$a_{2n+s-1} - a_1 = m_{2n+s-1,1}\,\pi, \qquad s = 1, 2, \ldots n-1.$$

Proceeding in this way, we can prove in general

$$a_s - a_1 = m_{s,1}\,\pi,$$

where $m_{s,1}$ is an integer; so that our proposition is proved.
Conversely since

$$\frac{Z}{a_1} = z + \frac{a_2}{a_1}z^2 + \cdots$$

is real, an extreme way is the x-axis, hence, of the function Z. Thus when an extreme way is a straight line, by the rotation of the axes, the line may become the x-axis; next rotating the X-axis, the series

becomes real; hence, *when the extreme way is a straight line, the corresponding curve of extreme value is also a straight line.*

7. Application to the modular function $J(\tau)$.

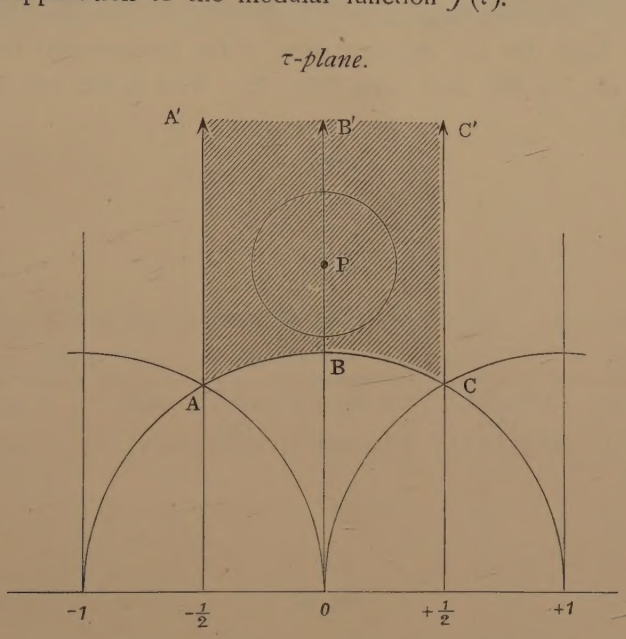

Fig. 7.

Fig. 7 shows the fundamental region of the modular function $J(\tau)$, in which we know that

$$\text{at } A,\ J = J\left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right) = 0,$$

$$\text{at } B,\ J = J(i) = 1,$$

$$\text{at } \infty,\ J = J(\infty) = \infty\ ,$$

and that the function takes real values on the lines AA', AB, BB' and on their homologous lines. Now take any point $P(\tau_0, J_0)$ on the line BB', then we have an expansion:

$$J - J_0 = a_1(\tau - \tau_0) + a_2(\tau - \tau_0)^2 + \ldots, \qquad a_1 \neq 0.$$

Putting $J - J_0 = Z,$

$$\tau - \tau_0 = iz,$$

it becomes $Z = b_1 z + b_2 z^2 + \ldots, \qquad b_1 \neq 0.$

When z takes real values, τ takes values on the line BB', therefore the corresponding values of J resp. of Z are real and the series is a real series; hence the x-axis resp. the line BB' is an extreme way of the function $J(\tau)$. So also is the line AA'; but the line AB is not an extreme way; for the representation of the fundamental triangle in the plane of J is the real axis (Fig. 8). Now if the arc AB is an

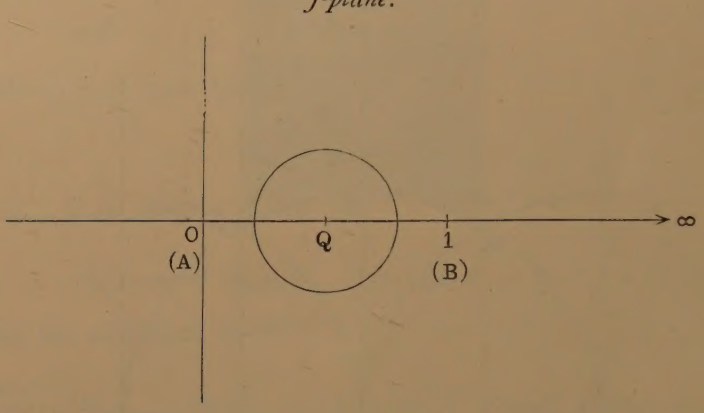

Fig. 8.

extreme way, then the part $\overline{01}$ of the real axis will be an extreme way of the inverse function $\tau(J)$. (§ 3). Since the extreme way is a straight line, the corresponding curve of extreme value must be also a straight line, (§ 6). But the line AB is an arc, i.e., the arc AB cannot be an extreme way of the modular function. The homologous lines of AA' resp. of BB' are extreme ways or not, according as they are straight or not, since the linear substitutions transform circle to circle but not in general centre to centre.

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